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Absorption Spectra of Some Organic Solutions in the Vacuum Ultraviolet

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(Received September 17, 1943)

A search for a suitable solvent for extending the absorption curves of some organic compounds into the vacuum ultraviolet led to the discovery that *n*-hexane and *n*-heptane give satisfactory transmission to 1700A, in 0.3-mm cells. The transmission limits of several solvents are given; and the absorption curves in this region are plotted for a number of organic compounds, showing especially the double-bond peak at 1840A from octene-3. It is demonstrated that a fluorite spectrograph of the Cario-Schmitt-Ott design is fast and convenient to use in such studies and is therefore well suited to routine quantitative analysis in this region (2500–1700A) when low dispersion (20A/mm) is acceptable.

WHILE studying the absorption spectra of the fatty acids in solution, we found that the most interesting part of the curves of the mono-olefin acids apparently lay beyond the region accessible to the quartz spectrograph. A search was therefore begun for solvents which would transmit farther into the ultraviolet, and a light source, absorption cell, and fluorite spectrograph were assembled so that solution spectra could be measured in the vacuum region.

As a result of this undertaking we were able to carry the spectra of the fatty acids to 1700A using saturated hydrocarbon solvents. These curves will be published elsewhere.[1] However, we think it worth while to present here separately the results of our studies on the transmission limits of various solvents and also the curves of some other organic compounds which were measured incidentally to this work. By showing the ease with which data can be obtained on solution spectra in the vacuum ultraviolet, we hope that other laboratories will be encouraged to work in this fascinating but relatively untouched field.

The curves given here (alcohols, ketones, an aldehyde, an ether, and an olefin) are of considerable interest for comparison with theoretical predictions about the electronic spectra of polyatomic molecules. It is to be noted, however, that since these were designed to be survey measurements, most of the samples were not specially purified; also that the measurements are in heptane solution instead of the theoretically more interesting vapor phase; and that the uncertainties in the values of ϵ are estimated at 20 percent. The curves are being presented now because it may be some time before we can repeat them with any higher accuracy, though we believe that with a little more study the errors in our method can be reduced to less than 5 percent.

The apparatus and procedure used in this work is being described in some detail; not because any

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[1] I. Rusoff, J. R. Platt, H. B. Klevens, and G. O. Burr, in preparation.

major element of the set-up is new, but because the assembly as a whole brings, we believe, three important new ideas to ultraviolet spectroscopy:

(1) the ultraviolet limit of routine measurements on solution spectra can be pushed to 1700A with saturated hydrocarbon solvents;

(2) the fluorite spectrograph can be as speedy and convenient in operation in the region 1700A–2500A, as the quartz spectrograph is in its own region (this point has been proved only for absorption spectra, but seems capable of easy extension to emission spectra);

(3) the fluorite spectrograph can be adapted for fast routine semi-quantitative and probably quantitative measurements when low dispersion is acceptable.

We hope that these ideas will overcome some of the prejudice of users of spectrochemical apparatus, such as chemists and biologists, against extending their measurements into the Schumann region; for this prejudice is based in great measure on the false belief that apparatus for vacuum region absorption measurements is always more complicated, more tedious to use, and more expensive than quartz instruments.

APPARATUS

Our experimental assembly is similar to that used by Scheibe.[2] A diagram of the essential parts of the apparatus is shown in Fig. 1. The light source L is a hydrogen discharge tube of the Urey[3] type; it draws about 0.8 amp. from the secondary of a 4-kw, 4400-v/220-v, General Electric transformer attached to the 220-v city lines in series with a variable ballast resistance of about 15 ohms. The primary circuit is closed by relay from a mercury switch attached to the handle of the water valve, so that the cooling water always flows when the discharge is running.

Light from the source passes through the absorption cell C shown in detail in Fig. 1A. The cell is formed by the gap between the two round lithium fluoride windows[4] 3 mm thick and 20 mm in diameter, which are sealed with Glyptal

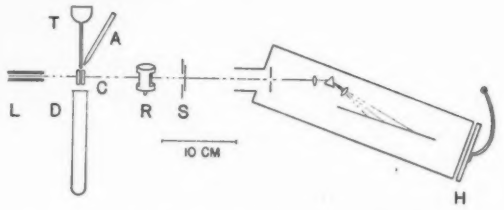

FIG. 1. Schematic diagram of experimental arrangement.

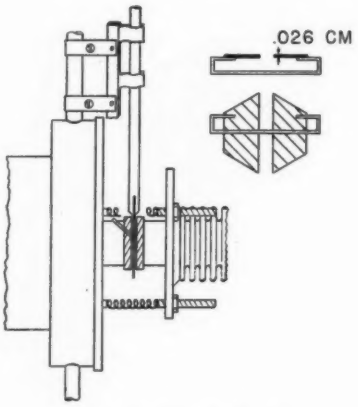

FIG. 1A. Detail of cell.

lacquer over the open ends of the Urey tube and the spectrograph vacuum system. The window on the spectrograph side is attached to a brass collar and plate as shown, flexibly joined to the spectrograph proper by a sylphon bellows for ease in alignment. By adjusting the tension of three springs which connect this brass plate to the water-jacket (on which the other window is mounted), the two windows can be pressed uniformly against the copper spacer which separates them. The absorbing liquid is allowed to run continuously through the cell from a capillary thistle tube T. This procedure was designed to minimize the effects of oxidation or photodecomposition on the chromophores. The surface tension of our solutions is adequate to keep the cell full of liquid if the gap is less than about $\frac{1}{2}$ mm; most of our work was done with a gap of 0.026 cm. The drippings are caught in a tube D for redistillation and recovery of the solvent. After finishing an exposure, the remaining liquid in the cell can be blown out with an air jet A and the cell rinsed with clean solvent.

After traversing the cell, the light is passed in succession through the photometric rotor R,

[2] G. Scheibe, Zeits. f. physik. Chemie **B5**, 355 (1929).
[3] H. C. Urey, Rev. Sci. Inst. **3**, 497 (1932).
[4] Obtained from Harshaw Chemical Company. The two windows together transmitted the light of the hydrogen arc to 1500A without appreciable loss. However, see the comment later on absorbing films.

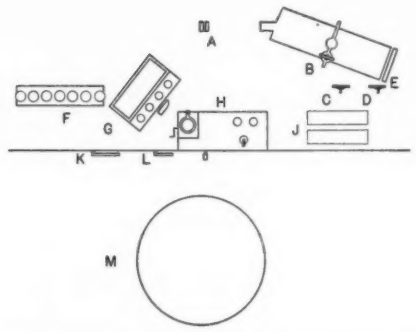

FIG. 1B. Assembly of controls for routine operation: *A*, cell; *B*, air inlet into spectrograph; *C*, switch for oil pump; *D*, switch for overhead light; *E*, hinged door on spectrograph; *F*, rack for clean thistle tubes; *G*, rack and shelf for test tubes or bottles of solution, plate racking control and indicator; *H*, stopwatch-shutter control, switches to set and operate photometric rotor; *J*, plate boxes; *K*, lever to operate cooling water and Urey tube; *L*, control for air jet; *M*, operator's seat.

previously described,[5] the shutter *S* (a small camera shutter set on "Bulb" and manipulated from outside the vacuum system through a sylphon), and the slit and optical system of a standard Cario-Schmitt-Ott fluorite spectrograph.[6]

This spectrograph was loaned to us by the University of Michigan, and we take this opportunity of expressing our thanks for their generosity. With this instrument, a single exposure maps the entire region from the visible to 1300A in good focus, with a dispersion of 40A/mm at 2200A and 13A/mm at 1500A; the numerical aperture is about *f*/10. The instrument takes four exposures on a plate $\frac{3}{4}$ in. by 4 in., the plate being racked down between exposures by an electromagnet controlled from outside the vacuum. The plate is put in or taken out in total darkness through a hinged door *H* (Fig. 1) over the end of the spectrograph; as the door must be opened and closed many times a day, it is sealed with Apiezon "Q" "vacuum putty." The small volume of the spectrograph (three liters) makes it possible to get a vacuum adequate for working to 1600A after only two minutes' pumping with a Welch Duo-Seal oil pump.

The spectra are recorded on Eastman Spectroscopic Plates Type 103–0 and Type I–0, Ultraviolet Sensitized. The plates are developed and fixed in rocking trays with time and temperature control, according to standard photometric procedures. They are handled in the solutions only with print tongs (which have had their ends slotted to grip the edges of the plates securely). The densities are measured on a Kipp and Zonen densitometer of the Moll type, which has been remodeled by Mr. P. A. Caldwell to permit horizontal and vertical movement of the plate. The logarithmic galvanometer scale reads photographic density directly, once the light intensity has been adjusted to give a standard "clear plate" deflection. (This feature facilitates graphing of gamma-curves.)

A Lucite scale is used to aid in locating wave-lengths on the plates. This scale was graduated by a ruling engine into convenient wave-length intervals, according to computations from comparator measurements on the spectra of Hg, Si, O_2, and H_2. The reference line used is a prominent line from the Urey tube (H_γ?), near the long wave-length limit of the emulsion. Wave-length positions on the emulsions are located for densitometry by using the Lucite scale and a hand lens, and are marked with a sharp steel stylus; positions can be duplicated by different workers to within 5A, which is adequate accuracy for the broad absorption maxima involved in these studies. (No fine structure was visible to the eye on any of our solution plates, although the resolution was good enough to show the fine structure in the Schumann bands of O_2.)

The determination of the absorption curve of a compound in solution involves computing for a series of wave-lengths the molar extinction ϵ:

$$\epsilon = E/ct,$$

where c is the concentration of the compound in moles/liter, t is the cell thickness in centimeters, and E is the extinction,

$$E = \log_{10}(I_0/I);$$

I_0 and I are the light transmitted at that wave-length through the solvent and solution, respectively, when the incident intensity is the same. In the present experiments, the extinction is determined as follows: Four exposures are made in quick succession, all of equal duration. The first two exposures are through the solvent,

[5] J. R. Platt, H. E. Clark, A. A. Cohen, and P. A. Caldwell, Rev. Sci. Inst. **14**, 85 (1943).
[6] H. Bomke, *Vakuumspektroskopie* (Barth, Leipzig, 1937), pp. 39–40.

one with the photometric rotor opening at 22° 34′; the second with a 52° 48′ opening; the third and fourth exposures are both through the solution with the rotor at 78° 55′. The time averages of intensities transmitted by the rotor are proportional to the angular opening; so if exposures 3 and 4 have the same density as exposure 1,

$$E = \log_{10}(78° 55'/22° 34') = 0.544,$$

while if 3 and 4 are identical with 2,

$$E = \log_{10}(78° 55'/52° 48') = 0.175.$$

If the density values are in the straight line region of the H-D curve of the emulsion, intermediate extinctions may be obtained by linear interpolation (graphical). In practice, extinctions from 0.20 to 1.00 are accepted, though the higher values are given less weight because of the possibility of systematic errors due to scattering in the spectrograph. Different workers can duplicate extinction determinations on one plate to 0.01.

Since ϵ may vary by a factor of more than a thousand from one wave-length to another, while the measurable range of E is small, several different concentrations of the compound must be used to map the curve completely. In the present work, plates are taken starting with the highest convenient concentration and then diluting this to $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{10}$, $\frac{1}{20}$, etc., until a concentration is reached at which the highest absorption maximum in the region is measurable; these changes in concentration from one plate to the next are small enough that several determinations of ϵ can be made at each wave-length.

The short exposures (15 to 60 sec.) and small cell make possible the mapping of ϵ over a 100A range (the average measurable region per plate) with as little as 1 cc of solution. However, in general, dilutions are made in 10 cc volumetric flasks with calibrated pipettes of 1 cc and larger. Weighings of solute are made on an analytical balance with an accuracy of better than 0.1 percent.

The whole spectrograph assembly is very compact, and well adapted for routine operation. After all of the switches and controls had been centrally located in front of the operator's stool (see Fig. 1B), it was found possible to train inexperienced men in a short time to turn out five or six plates per hour. A time analysis for one plate would look somewhat as follows:

Evacuating spectrograph	2 min.
Four 30-sec. exposures	2 min.
Changing rotor, replacing thistle tubes, pouring solution	2 min.
Removing plate, inserting new one	1 min.
Total spectrograph time per plate	7 min.

A time lapse of this magnitude, even when combined with the processing and densitometry time, is not incompatible with the possible use of such apparatus for production control. In this connection it should be emphasized that a fluorite apparatus of the Cario-Schmitt-Ott design is cheaper, smaller, and more portable than a small quartz instrument. Chemical spectroscopists seem not to have realized the possibilities of fluorite spectrographs for routine industrial control and testing when chromophores of this wave-length region (see below) are involved. However, industrial application must await the elimination of troublesome absorbing films on the windows such as those mentioned below.

In our work, extinction values above 2130A are checked on a medium Hilger E2 quartz spectrograph, using a 5-mm absorption cell of standard type, with another Urey tube as light source. These plates are calibrated by use of a step-slit,[7] and wave-lengths are located with a Lucite scale made similarly to the scale used with the fluorite plates. The solvent exposures are reduced in intensity by a sector disk of conventional type, so as to give them a density equivalent to an extinction of 0.400; solution exposures above or below this density then have extinctions correspondingly below or above 0.400, the correction being found from the gamma-curve determined for each plate.

This check by the quartz instrument has enabled us to place more confidence in the fluorite determinations, for the molecular absorption values from the quartz usually fall within the scatter pattern of the values from the fluorite. The quartz values can be completely redetermined, starting with fresh samples of solute, with less than 5 percent discrepancy.

[7] W. R. Brode, *Chemical Spectroscopy* (Wiley, New York, 1939), p. 39.

TABLE I.

Impurity in sample	Unknown	Checked by homologues
Weighing and dilution	<1 percent	
Evaporation or oxidation	Unknown	Samples are run quickly
Small bubbles in liquid	Unknown	Reproducible (exps. 3 and 4 agree well)
Irreg. cell faces and errors in thickness	<3 percent	
Absorption by solvent	Unknown	Lowers apparent E for high conc. near solvent transmission limit
Emulsification	Unknown	Turbidity was watched for
Arc fluctuations	<1 percent	Av. ammeter reading over 30-sec. intervals is very constant
Rotor error	<1 percent	
Spectrograph scatter	Small	ϵ from high E not systematically different from ϵ from low E
Emulsion flaws	Unknown	More common in sens. plates
Faulty processing	Unknown	Presumably constant over a given plate.
Wave-length calibration	<5A	
Densitometry	<2 percent	Reproducible to this figure

TABLE II. Transmission limits of various solvents in cell 0.3 mm thick.

	Limit	Other Meas.
1. water	1790A	1792[a] 0.5 mm liq. 1780[b] vapor
2. potassium hydroxide, 0.05 m in water	2050	
3. methyl alcohol	1890	
4. ethyl alcohol	1890	2039–1870 } [c] vapor below 1570 } 1850[d] 0.1 mm liq.
5. *n*-hexane	2020 }	
6. *n*-hexane	1705 }	1700[e] vapor; (photo-
7. *n*-heptane	1960 }	graph shows abs. to
8. *n*-heptane	1705 }	1700)
9. *n*-heptane	1705 }	
10. iso-octane	1780	
11. "Skelly-solve"	2250	
12. ethyl ether	1980	1900[f] vapor
13. ethyl ether	1960	
14. acetone	2000	agrees[g] liq.
15. ethyl alcohol, 10 percent by vol. in hexane	1780	
16. ethyl alcohol, 1 percent by vol. in hexane	1710	
17. iso-octane, 10 percent by vol. in hexane	1730	

[a] T. Lyman, Nature **84**, 71 (1910).
[b] G. Rathenau, Zeits. f. Physik **87**, 32 (1933).
[c] See reference 16 of text.
[d] See reference 2 of text.
[e] E. P. Carr and H. Stücklen, Zeits. f. physik. Chemie **B25**, 57 (1934).
[f] See reference 14 of text.
[g] See reference 12 of text.

Notes on solvents in Table II:
1. From the Physics Department still.
2. A. R. grade, "acetone-free."
3. C. P.
4. Constant boiling mixture (5 percent water), redistilled.
5. Eastman Kodak Company, Eastman Grade; same limit after shaking with H_2SO_4 until acid was clear.
6. Same, after refluxing with chlorosulfonic acid 5 hours, and passage through a long silica gel column 3 times. (See J. Research Nat. Bur. Stand. **9**, 457 (1932).)
7. Eastman Kodak Company, Eastman Grade.
8. Same, after treatment given in note 5.
9. California Chemical Company (subsidiary of Westvaco Chlorine Corporation) after shaking with sulfuric acid for 24 hours.
10. Röhm and Haas Company; same limit after treatment of 5 (but the H_2SO_4 never comes off as clear as with n-heptane); same limit after treatment of 6.
11. Skelly Oil Company; three fractions with minute differences in boiling points gave same limit, after treatment of 5.
12. C. P.; redistilled.
13. Anaesthesia ether, freshly opened (contains some alcohol); same limit after purification according to three different methods (b.p. 34.5°C):
    a. Ber. Deut. Chem. Ges. **59**, 1774 (1926).
    b. No. 4, Analyst **58**, 335 (1933).
    c. Bull. Soc. Chem. Biol. **6**, 299 (1924).
14. C. P.; redistilled.
15, 16, 17. *n*-Hexane of 6 for solvent; ethyl alcohol of 4, iso-octane of 10.

SOURCES OF ERROR

Some possible sources of error in the fluorite work are listed in Table I, with an estimate of their importance and some comments.

None of these errors seems adequate to account for the widely divergent values of ϵ (20 percent to 50 percent off) given by occasional plates, except possibly faulty technique in processing the small fluorite plates.[8] If this is really the difficulty, then when it is corrected, there seems to be no reason why a reproducibility as good as 5 percent should not be attained.[9] We are working to achieve this goal.

It should be mentioned that our work was hampered by the development of an absorbing film on the window surface within the spectrograph after a few hours of operation. This film could usually be removed by opening the system and swabbing the window with alcohol or heptane, though once or twice it proved impossible to take away the absorbing material even by grinding and repolishing the window surface. Several weeks were devoted to unsuccessful attempts to find the cause of these films and

[8] Dr. H. B. Vincent has mentioned in private conversation that a likely source of trouble in ultraviolet sensitized plates lies in failure to clear the fluorescent sensitizer completely away before development. To avoid this trouble, he suggests that the standard ethylene chloride rinse be followed immediately by acetone, then by a water rinse, and then by developer, without allowing the plate to dry at all between these solutions. We are trying this technique but a comparison of results is not yet available.

[9] Dr. Vincent also says he has been able to reproduce emission spectra analyses to 5 percent, using 103–0 U.V. Sens. and I–0 U.V. Sens. plates. This large error (compared to about 1 percent for emission spectra work using unsensitized plates) he attributes mostly to statistical fluctuations in the density of the photometered area, due to the large grain of the Type I and 103 emulsions, and possibly also due to a point-to-point variation in the effect of the sensitizing layer.

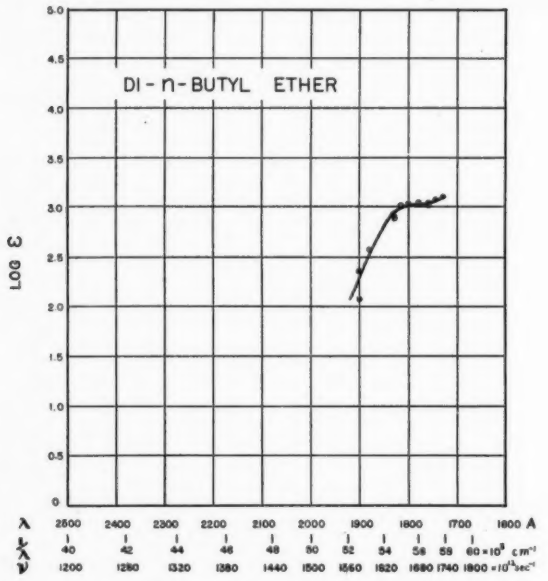

FIG. 2. Student preparation, organic chemistry laboratory, University of Minnesota ("org. prep."); b.p. 141.5–142°C (corrected to standard pressure).

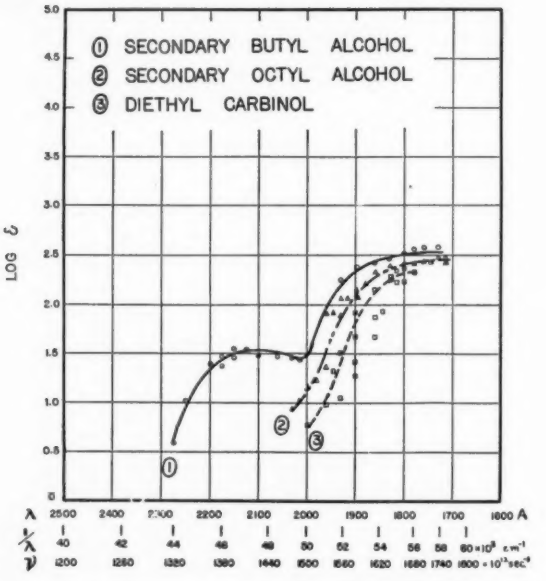

FIG. 4. (1) Org. prep.; b.p. 99.7–100.7. (2) Merck and Company, b.p. 177.5–178. (3) Eastman Kodak Company; b.p. 117.7–118.2.

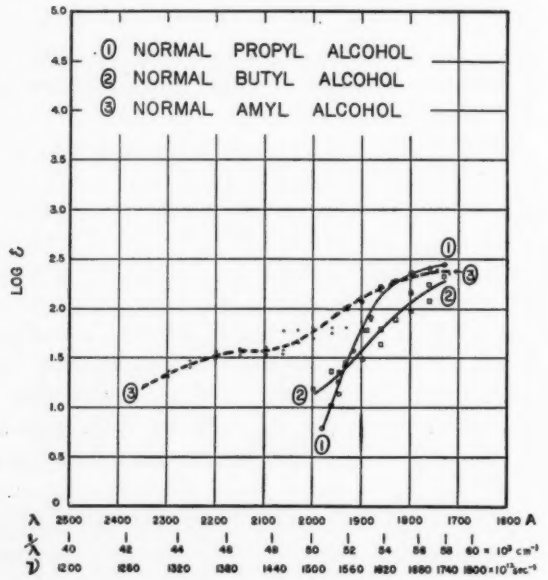

FIG. 3. (1) Eastman Kodak Company; b.p. 97.3. (2) Org. Prep. (see legend to Fig. 2); b.p. 117.6–117.8. (3) Org. prep.; b.p. 138.

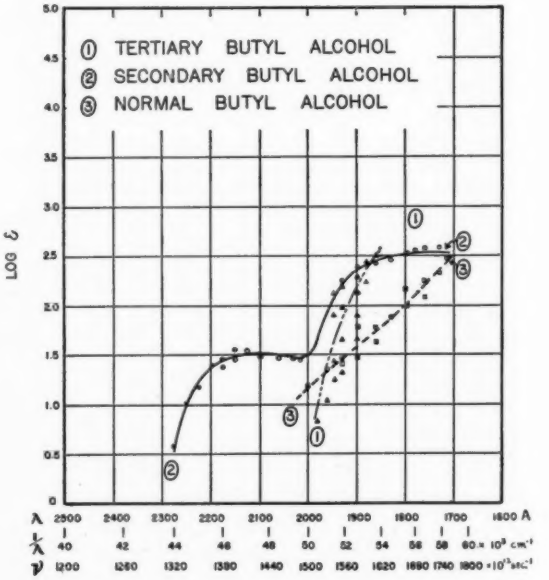

FIG. 5. (1) Org. prep.; b.p. 84–85. (2) See Fig. 4, ref. 1. (3) See Fig. 3, ref. 2.

prevent them. It is believed that they arose from some unfavorable combination of the vapors of the oils and waxes in the spectrograph. We believe this film is not an appreciable source of error in the curves given here because on each plate the effect of the film must be approximately constant for all exposures.

SOLVENTS

When we undertook to study the absorption curves of the fatty acids to 1700A, we were not

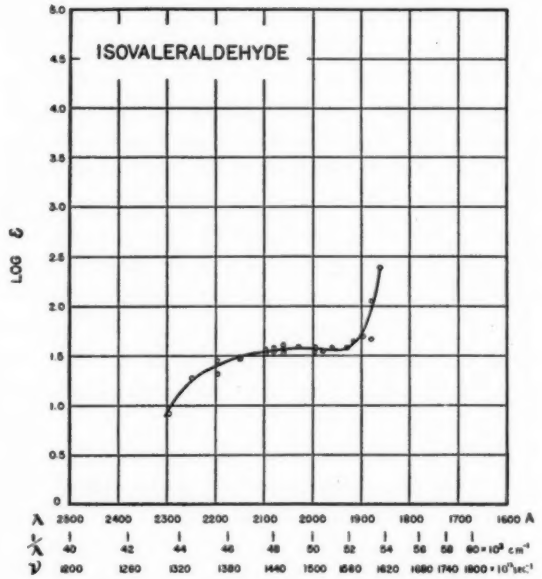

FIG. 6. Eastman Kodak Company; b.p. 92–92.5

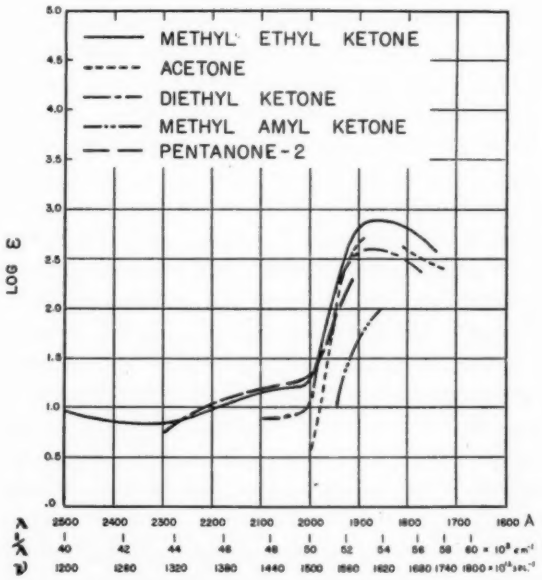

FIG. 7. *MEK*, Eastman Kodak Company; b.p. 79.5. *A*, same curve from two samples, one C.P., the other, C.P. purified by NaI method; b.p. 56.5. *DEK*, Eastman Kodak Company; b.p. 101.5. *MAK*, org. prep.; b.p. 149.5–150. P-2, b.p. 102.

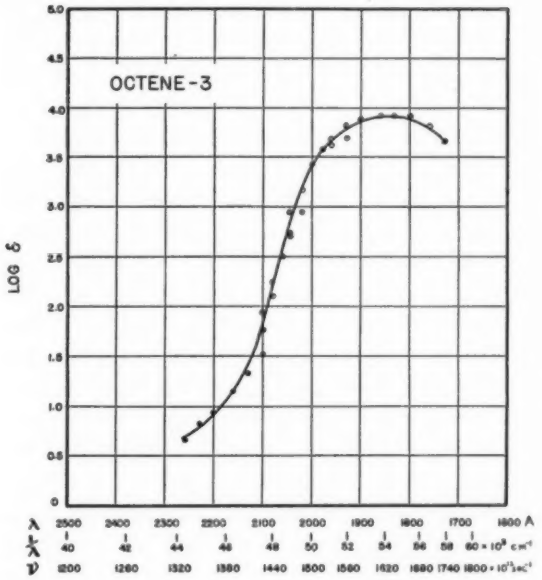

FIG. 8. Supplied by the courtesy of Dr. F. L. Greenwood of the Department of Biochemistry, who prepared it by the method of Wibaut and Gitsels, Rec. trav. Chim. **59**, 947 (1940), obtaining exactly the expected boiling point and refractive index ($n/20° = 1.4133$). After the octene was taken from a sealed ampoule and the refractive index checked, the sample was run immediately.

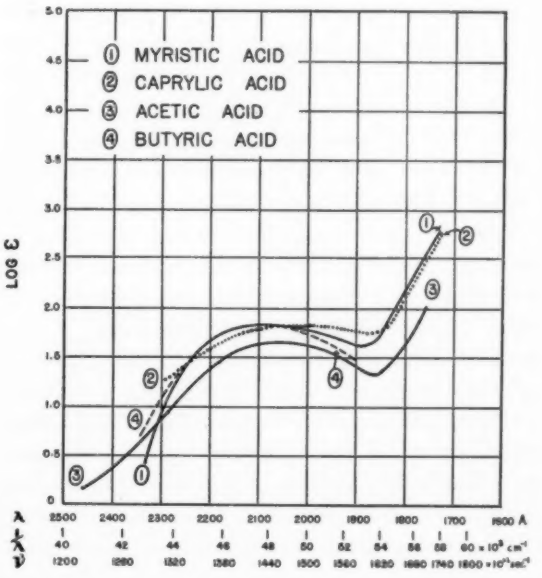

FIG. 9. Curves from reference 1.

certain of finding a suitable solvent transparent to this limit.[10] We therefore measured the transmission limits of a number of pure liquids in our cell. These limits are shown in Table II; they are

[10] G. Scheibe, F. Povenz, and C. F. Linstrom, Zeits. f. physik. Chemie **B20**, 283 (1933). These authors mention that no solvent is known at that time which will transmit below 1800A. Recently, Emma P. Carr has made substantially the same comment in a private communication, excepting, however, "thin films."

the limits of the plate blackening for reasonable exposures, by visual inspection. In the last column of Table II are given some previous measurements on these compounds, of the transmission limits for the liquid and the position of the longest wave-length absorption measured in the vapor phase. Our limits for the liquid state agree rather well with these previous values.

As would be expected, the limits for the liquid phase lie fairly close to the beginning of the first bands of the same compound in vapor phase (and in the case of alcohol even *below* the first recorded vapor bands!). This fact suggests that, in the search for better solvents for the Schumann region, little will be gained by further purification of the compounds listed here, and a study must instead be made on different compounds using the information gained here as a guide. The cases of ether and the alcohols, for example, seem to show that an oxygen atom in the molecule decreases the transparency. Also iso-octane seems not as transparent as the straight-chain hydrocarbons. Therefore, the best solvents in this region are likely saturated pure hydrocarbons, unbranched.

We did not continue our solvent purification and measurement after finding *n*-heptane was satisfactory for our work. However, the saturated cyclic hydrocarbons, which are missing from Table II, also deserve to be investigated carefully in any systematic search for Schumann solvents. The one paper on the ultraviolet absorption of these compounds which has come to our attention,[11] gives a molar extinction coefficient for cyclopropane (determined for the vapor phase) which is somewhat higher at the shortest wave-lengths studied (1890A) than our estimated value of the coefficient for *n*-heptane in this neighborhood. It remains to be determined whether the higher saturated cyclics will show the same behavior, or whether they will become more transparent as they become more stable.

The transmission limits for the liquid phase can in general be improved only slightly by using a thinner cell, because the absorption curve of the solvent is usually very steep in the neighborhood of the limit. Ley and Arends,[12] for instance, only obtained about 100A shift in the limit of acetone on decreasing their cell thickness from 0.1 mm to 1/40 of that value. We found a negligible change in the limit of *n*-heptane until our cell thickness became less than 0.1 mm, which is inconveniently thin for solution studies.

It is evident from Table II that slight traces of impurity may change markedly the transmission of a solvent; if the impurity is uncontrolled, quantitative work may be impossible. In our work in lipid compounds, for example, it was found that traces of benzene in the solvent and traces of lye in the solutes had to be completely removed.

The solvent finally decided on as adequate for our project is the *n*-heptane obtained from California Chemical Company. It and the purified *n*-hexane are equally superior, but the latter is considerably more expensive. The cost of this *n*-heptane in the small amounts needed for these analyses is quite moderate. This liquid as it comes from the container is very clean and transmits almost as well as it does after treatment; it scarcely stains the sulfuric acid used in the treatment.

n-Heptane has the drawback that it is a poor solvent for many compounds; we have been unable to run several interesting curves, notably those of the aldehydes, for this reason. However, when compounds are soluble in it (or absorb so strongly that only dilute solutions are needed), *n*-heptane has the advantages that it is non-polar and that its boiling point is well above room temperature and so errors of concentration due to evaporation are small. Higher solubility is obtained with some solutes (not given here) by adding a little alcohol or iso-octane to the *n*-heptane. The transmission limits of some mixed solvents are shown in Table II. Of course, in such cases, if the added component of the solvent is polar, the mixture probably also affects absorption like a polar solvent.

Water was used as a solvent in some preliminary studies, until it was found that the cell faces were etched by it and had to be repolished frequently; this difficulty would have been much less troublesome if the windows had been of fluorite, because of its lower solubility in water, but unfortunately we were unable to obtain any of this material.

[11] A. A. Ashdown, L. Harris, and R. T. Armstrong, J. Am. Chem. Soc. **58**, 850 (1936).
[12] H. Ley and B. Arends, Zeits. f. physik. Chemie **B12**, 132 (1931).

ABSORPTION CURVES

The absorption curves of the compounds studied are shown in Figs. 2–9. The molar extinction values are plotted logarithmically to show the detail of the lower parts of the curves. The experimental points are omitted on Figs. 7 and 9, to avoid confusion; the scatter of the points on these curves is comparable to that in other figures. We believe the curves are accurate to about 20 percent in absolute value (0.1 log unit).

Most of the curves do not cover the whole wave-length region for two reasons. At long wave-lengths, they cannot be plotted because the low absorptions demand higher concentrations than the solubility in heptane permits. (And methyl alcohol, *n*-butyraldehyde, iso-butyraldehyde, and *n*-propionaldehyde could not be run at all because the solubilities were too low.) At short wave-lengths, plates on several curves were defective because a mistake was made in estimating exposure time, and was not discovered until the plates came to be read some days later. The pressure of other work prevented us from obtaining and running new samples of these compounds.

These survey curves were run without elaborate purification, as we hoped to discover impurities by comparison of the curves of a family for similarity and dissimilarity. In this aim we were partially successful. Thus, in secondary butyl alcohol (Fig. 4), an impurity must be invoked to explain the peak at 2125A; and in *n*-amyl alcohol (Fig. 3) the absorption in the same region also seems out of line. By the same reasoning, the curve of *n*-butyl-di-methyl carbinol had to be omitted here because it differed considerably from curves of the other alcohols. In Fig. 9, similarly, the butyric acid curve is one of two obtained in this laboratory on different samples; the other curve was eliminated because it diverged considerably from the curves of the other saturated acids, and from the measurements of Henri,[13] at longer wave-lengths.

There is almost no literature on the Schumann spectra of the compounds in Figs. 2–5. However, the curve of di-*n*-butyl ether in Fig. 2 agrees qualitatively with the vapor absorption of di-ethyl ether,[14] which has several maxima in the region from 1900A to 1820A, and a minimum at 1750A. Di-ethyl ether vapor was also studied by Price, who gives a photograph[15] of the spectrum, showing absorption beginning at 1920A, with principal maxima near 1875A and 1710A and a minimum at 1790A.

Among the alcohols (Figs. 3, 4, 5) only the secondary alcohols of Fig. 4 show any marked regularity. They seem to have a secondary maximum or "step-out" on the curve, centering between 1800A and 1900A. This agrees roughly with Leifson's discovery[16] of vapor maxima between 2040A and 1870A in ethyl alcohol, and with Brode's assignment of a peak at 1860A to the O—H bond.[17] This step-out, however, is not so clear on the curves of tertiary or normal alcohols, and therefore may be dependent on the number of substituents on the carbinol.

There has been more previous work on the chromophores of Figs. 6–9. The qualitative agreement of Fig. 6 with the vapor spectrum given by Scheibe, Povenz, and Linstrom[10] for acetaldehyde is good—the vapor has a strong peak near 1805A, and some lower maxima at longer wave-lengths. The agreement with previous solution studies is somewhat uncertain, as our curve lies below Henri's earlier curves on propionaldehyde and butyraldehyde in hexane (but has the same shape),[18] but lies well above both of the two divergent curves later given by him for propionaldehyde.[19]

The ketone curves (Fig. 7) all have the same unmistakable maximum at 1860A, with a suggestion on one of the methyl ethyl ketone plates that this maximum may consist of two peaks about 70A apart. The absorption above 2000A of all these compounds must be due to impurities, for the curves in this region lie above those given by Ley and Arends[12] for acetone and by Henri[20] for methyl iso-butyl ketone (both curves in hexane). An impurity of 0.1 percent of conju-

[13] V. Henri, *Etudes de Photochimie* (Gauthier-Villars, Paris, 1919), p. 95.

[14] G. Scheibe and H. Grieneisen, Zeits. f. physik. Chemie **B25**, 52 (1934).

[15] W. C. Price, J. Chem. Phys. **3**, 256 (1935).

[16] S. W. Leifson, Astrophys. J. **63**, 73 (1926).

[17] See reference 7, p. 130.

[18] See reference 13, p. 85.

[19] *International Critical Tables* V (McGraw-Hill, New York, 1929), Fig. 29, p. 365; Fig. 73, p. 374.

[20] See reference 19, Fig. 68, p. 372.

gated material would be enough to raise their curves to the values found here. From 2000A to 1800A, the limit of Ley and Arends' curve, our acetone curve duplicates theirs within our experimental error. The ketone peak is confirmed by the vapor studies of Scheibe, *et al.*,[10] and Noyes and his co-workers,[21] who report absorption structures in the region from 1800A to 1950A for acetone. The bands given by Duncan and his co-workers[22] for methyl ethyl ketone vapor, on the other hand, are near 1710A and 1970A and are farther away from the peak of Fig. 7.

The high broad maximum of octene-3 (Fig. 8) is evidently the double-bond maximum found by Carr and Stücklen[23] for hexene-3 and heptene-3 in vapor phase. The maximum, however, is shifted in our heptane solution some 60A toward the visible. The peak is a broad continuum for the vapor but is probably further broadened here by the contribution of several smaller vapor peaks near 2000A. The octene-3 curve will be compared elsewhere[1] with the spectra of some unsaturated fatty acids. It will be shown there that this peak is faithfully reproduced in other compounds containing a double bond weighted at both ends, and that the absorption of double bonds and distant acid radicals in the same molecule is additive within our experimental error. The double-bond peak is the strongest one we have found in this region. Very likely it would be the most interesting maximum for industrial spectrochemical applications of fluorite spectroscopy.

The saturated fatty acids shown in Fig. 9 are part of the paper mentioned above,[1] but it will be noted here that they are in excellent agreement with published curves on these compounds, such as that of Scheibe *et al.*[10] for acetic acid vapor; that of Ley and Arends[24] for acetic acid in hexane solution; and the curve of Henri[13] for butyric acid. This agreement is to be expected because the study of these acids was the main purpose of our project, and some pains were taken to obtain complete curves on very pure samples.

A comparison of the experimental curves given here with some theoretical predictions is to follow shortly.

CONCLUSION

We have shown that (1) absorption spectra of solutions can be extended to 1700A, (2) the fluorite spectrograph as an instrument for routine analysis can be made convenient and fast, and (3) probably can be made quantitative at the same time, in the range 2500–1700A. The only solvents found so far for which a 0.3-mm thickness will transmit to 1700A are purified *n*-heptane and *n*-hexane, the samples we obtained of the former being cheaper and easier to purify. The curves of some simple organic chromophores are shown. A concentrated development program on the industrial exploitation of solution spectra in this region would apparently be quite profitable.

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[21] W. A. Noyes, Jr., A. B. F. Duncan, and W. M. Manning, J. Chem. Phys. **2**, 717 (1934).
[22] A. B. F. Duncan, V. R. Ells, and W. A. Noyes, Jr., J. Am. Chem. Soc. **58**, 1454 (1936).
[23] E. P. Carr and H. Stücklen, J. Chem. Phys. **4**, 760 (1936).
[24] H. Ley and B. Arends, Zeits. f. physik. Chemie **B17**, 177 (1932).

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The Electrostatic Contribution to Hindered Rotation in Certain Ions and Dipolar Ions in Solution. I

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From experimentally determined dissociation constants and structural parameters, effective dielectric constants are calculated for a few substances. This allows in each case an estimate of the electrostatic contribution to hindered rotation. For dithionic acid, whose dissociation constants are not known, a reasonable D_E must be assumed in order to make the same calculation for the various possible ionic species. The influence of these results on ionic equilibria in dithionic acid is then discussed in some detail.

I. INTRODUCTION

IN order to study electrostatic influences on the dissociation of certain acids, let us begin by considering the general equilibrium

$$A_a(\text{acid}) \rightleftarrows A_i(\text{ion}) + H^+$$

for which the usual thermodynamic dissociation constant (we assume sufficiently dilute solutions throughout) is

$$K = c_i x / c_a, \tag{1}$$

where x is the hydrogen ion concentration.

In general, there will be charges located in the molecules A_a and A_i. In the discussion below we shall not be concerned explicitly with permanent charges in molecules (e.g., the permanent positive formal charge on the phosphorus atom of phosphoric acid; the effects of such charges are included in K^0, below), but rather only in those charges which may be lost (positive charges) or gained (negative charges) by the dissociation of a proton.

Let $\theta_1, \theta_2, \cdots \theta_n$ be variable angles (of rotation about bonds) which must be specified in order to locate these charges in A_a and A_i. Associated with an assignment of $\theta_1, \theta_2, \cdots \theta_n$ are electrostatic potential energies $U^a(\theta_1, \cdots)$ and $U^i(\theta_1, \cdots)$, which include interactions between all non-permanent charges.

In addition to electrostatic potential energies, there will in general be additional potential energy functions $V^a(\theta_1, \cdots)$ and $V^i(\theta_1, \cdots)$ of the type known to hinder rotation in molecules in the gas phase. These restricting potentials are now believed to be of a quite local (to the bond about which rotation is inhibited) character, so that we make the following assumptions: (1) $V^a = V^i = V$, since A_a and A_i differ only by a peripheral proton; (2) V is essentially the same in solution as in the gas phase.[1]

The species A_a may exist (classically) in an infinite number of configurations, depending on $\theta_1, \cdots \theta_n$. For each such configuration there is an equilibrium of the type

$$A_a(\theta_1, \cdots) \rightleftarrows A_i(\theta_1, \cdots) + H^+$$

involving the corresponding form of A_i. Let $s_a(\theta_1, \cdots)$ and $s_i(\theta_1, \cdots)$ be the concentrations of A_a and A_i, respectively, at $\theta_1, \cdots \theta_n$. Then, if we write $k(\theta_1, \cdots)$ for the equilibrium constant of the above reaction,

$$k(\theta_1, \cdots) = s_i(\theta_1, \cdots) x / s_a(\theta_1, \cdots). \tag{2}$$

In addition to equilibria of this type between A_a and A_i for all possible values of $\theta_1, \cdots \theta_n$, there exists a Boltzmann distribution among the A_a and another among the A_i, so that

$$s_a(\theta_1, \cdots) = \frac{c_a \exp\{-[U^a(\theta_1, \cdots) + V(\theta_1, \cdots)]/RT\}}{\int_0^{2\pi} \cdots \int_0^{2\pi} \exp\{-[U^a(\theta_1, \cdots) + V(\theta_1, \cdots)]/RT\} d\theta_1 \cdots}, \tag{3}$$

[1] The author is indebted to Professor K. S. Pitzer for a very helpful discussion of this point. See footnote 3.

$$s_i(\theta_1, \cdots) = \frac{c_i \exp\{-[U^i(\theta_1, \cdots) + V(\theta_1, \cdots)]/RT\}}{\int_0^{2\pi} \cdots \int_0^{2\pi} \exp\{-[U^i(\theta_1, \cdots) + V(\theta_1, \cdots)]/RT\} d\theta_1 \cdots} \tag{4}$$

Combining Eqs. (1), (2), (3), and (4),

$$K = k(\theta_1, \cdots) \exp\{-[U^a(\theta_1, \cdots) - U^i(\theta_1, \cdots)]/RT\} \times \frac{\int_0^{2\pi} \cdots \int_0^{2\pi} \exp\{-[U^i(\theta_1, \cdots) + V(\theta_1, \cdots)]/RT\} d\theta_1 \cdots}{\int_0^{2\pi} \cdots \int_0^{2\pi} \exp\{-[U^a(\theta_1, \cdots) + V(\theta_1, \cdots)]/RT\} d\theta_1 \cdots} \tag{5}$$

Since K and the definite integrals appearing in Eq. (5) are independent of $\theta_1, \cdots \theta_n$, it is necessary that the first line of the right-hand member of Eq. (5) be also equal to a constant, which we shall designate by K^0. Thus,

$$K = K^0 \frac{\int_0^{2\pi} \cdots \int_0^{2\pi} \exp\{-[U^i(\theta_1, \cdots) + V(\theta_1, \cdots)]/RT\} d\theta_1 \cdots}{\int_0^{2\pi} \cdots \int_0^{2\pi} \exp\{-[U^a(\theta_1, \cdots) + V(\theta_1, \cdots)]/RT\} d\theta_1 \cdots} \tag{6}$$

and

$$k(\theta_1, \cdots) = K^0 \exp\{-[U^i(\theta_1, \cdots) - U^a(\theta_1, \cdots)]/RT\}. \tag{7}$$

It is evident from the form of Eq. (7) that K^0 is the electrostatically "unperturbed" value of K that would obtain in the absence of interactions between non-permanent charges in A_a and A_i ($U^a = U^i = 0$; $K = k = K^0$).

We shall consider in the present paper substances for which only one rotational angle θ is involved. We assume, conventionally, sinusoidal curves for U^i, U^a, and V, in which the potential barriers are $U_0{}^i$, $U_0{}^a$, and V_0. Being electrostatic potential energies, $U_0{}^i$ and $U_0{}^a$ depend not only upon the structural parameters of A_i and A_a, but also upon an effective dielectric constant[2] D_E which we assume here to be a constant, independent of θ (D_E is thus an average value over θ).

Evidently the point of view adopted in deriving Eqs. (6) and (7) necessarily leads to the same dielectric constant being involved in the two equations; intuitively, one might have expected otherwise.

For several cases in which all other parameters in Eq. (6) are known,[3] we shall calculate D_E and thence the electrostatic potential barriers. For dithionic acid, whose dissociation constants are not known, we shall guess a value of D_E in order to approximate the extent of electrostatic hindered rotation in this acid and its various possible ions.

The simplifying assumption is made that the two positive charges in the ethylene diammonium ion are point charges located on the nitrogen atoms. For each carboxylate group of the oxalate ion, we take one-half an electronic charge on each oxygen atom. The two assumptions above are also used in the amino acids considered. In dithionate ion, we assume an electronic charge on each oxygen atom and a double positive charge on each sulphur atom.[4,5]

With the exception of 1.50A for the C−C bond distance in oxalic acid[6] and 1.53A for the same

[2] J. G. Kirkwood and F. H. Westheimer, J. Chem. Phys. 6, 506, 513 (1938).

[3] V_0 may be estimated from known potential barriers of related substances in the gas phase; actually, since the calculations to be made are very insensitive to V_0, we shall merely carry them out in most cases for both $V_0 = 2000$ and 3000 cal./mole.

[4] A. Kossiakoff and D. Harker, J. Am. Chem. Soc. 60, 2047 (1938).

[5] G. E. K. Branch and M. Calvin, *The Theory of Organic Chemistry* (Prentice-Hall, Inc., New York, 1941).

[6] This is an average of two conflicting values appearing in the literature [see J. M. Robertson and I. Woodward,

TABLE I.

	U'	V
	$M/2$ $\quad \frac{1}{2}U_0 \cos f(\theta)$	
Ethylene diamine	$0.3278+0.0567 \cos \theta$	const.$+\frac{1}{2}V_0 \cos 3\theta$
Oxalic acid	$0.3277+0.0041 \cos 2\theta$	const.$+\frac{1}{2}V_0 \cos 2\theta$
α-Amino acids	$-0.3223-0.0053 \cos 2\theta$	const.$+\frac{1}{2}V_0 \cos 6\theta$
Dithionic acid, A_{14}	$0.2834+0.0434 \cos \theta$	const.$+\frac{1}{2}V_0 \cos 3\theta$
A_{124}	$0.5517+0.0415 \cos (\theta-\pi/3)$	const.$+\frac{1}{2}V_0 \cos 3\theta$
A_{1234}	$0.8351+0.0019 \cos 3\theta$	const.$+\frac{1}{2}V_0 \cos 3\theta$
A_{1245}	$1.118+0.0453 \cos \theta$	const.$+\frac{1}{2}V_0 \cos 3\theta$
A_{12345}	$1.670+0.0038 \cos 3\theta$	const.$+\frac{1}{2}V_0 \cos 3\theta$
A_{123456}	$2.505+0.0057 \cos 3\theta$	const.$+\frac{1}{2}V_0 \cos 3\theta$

Numerical values are in units of A^{-1}.

distance in the amino acids,[7] we shall employ[7] 1.54A for the C−C distance, 1.25A for C−O, 1.41A for C−N, 118° for the C−C−O angle, and 112° for C−C−N. The values for dithionic acid are:[8] S−S distance, 2.06A; S−O distance, 1.50A; all angles tetrahedral.

Calculations and data[9] for oxalic acid and ethylene diamine are for 20°C; all others[7] are for 25°C.

II. POTENTIAL FUNCTIONS

The six oxygen atoms of dithionic acid may be numbered such that, in a lined up position, 1 and 4, 2 and 5, and 3 and 6 are paired off, and 1, 2, and 3 successively eclipse 4 as θ increases. Let, say, A_{14} represent the species in which protons have been dissociated from positions 1 and 4 but not from positions 2, 3, 5, and 6, etc.

In Table I are listed the molecules to be considered here in which electrostatic hindered rotation occurs, and the nature of the approximate potential functions in each case. The numerical values have been calculated from the bond distances and angles. The units are A^{-1}. D_E must first be obtained in order to convert A^{-1} into cal./mole. U' in Table I is that part of U exclusive of interactions between charged atoms bonded to the same atom. That is, $U-U'$ is a constant, independent of θ. $U=U'$ for all substances treated here except some forms of dithionic acid (we need not be concerned with the interaction between the half electronic charges in the carboxylate groups since this is included in K^0).

In Table I,

$$M=U'_{\max}+U'_{\min},$$
$$U_0=|U'_{\max}|-|U'_{\min}|. \tag{8}$$

We shall write

$$M/2RT=m/2, \quad U_0/2RT=u/2,$$
$$V_0/2RT=v/2. \tag{9}$$

In performing the integrations of the functions in Table I, called for in Eq. (6), we make use of the following properties of Bessel functions:[10]

$$I_s(-a)=(-1)^s I_s(a),$$
$$e^{a\cos n\theta}=I_0(a)+2\sum_{s=1}^{\infty} I_s(a)\cos sn\theta,$$

where $I_n(a)$ is a modified Bessel function of the first kind. Thus, in particular,

$$\int_0^{2\pi} e^{a\cos n\theta}d\theta=2\pi I_0(-a)=2\pi I_0(a), \tag{10}$$

$$\int_0^{2\pi} e^{a\cos n\theta+b\cos 3n\theta}d\theta$$
$$=2\pi[I_0(a)I_0(b)+2\sum_{s=1}^{\infty} I_{3s}(a)I_s(b)], \tag{11}$$

$$\int_0^{2\pi} e^{a\cos(\theta-\pi/3)+b\cos 3\theta}d\theta$$
$$=2\pi[I_0(a)I_0(b)+2\sum_{s=1}^{\infty}(-1)^s I_{3s}(a)I_s(b)]. \tag{12}$$

J. Chem. Soc. 1817 (1936); and S. B. Hendricks and M. E. Jefferson, J. Chem. Phys. 4, 102 (1936)]. There is some evidence (see Robertson and Woodward) of partial carbon-carbon double bond character in oxalic acid, which would also tend to restrict rotation, but with the potential minimum in the planar configuration. This possibility is not taken into account here.

[7] E. J. Cohn and J. T. Edsall, *Proteins, Amino Acids and Peptides as Ions and Dipolar Ions* (Reinhold Publishing Corporation, New York, 1943).

[8] M. L. Huggins and G. O. Frank, Am. Mineral. 16, 580 (1931).

[9] G. Schwarzenbach, Helv. Chem. Acta 16, 522 (1933).

[10] Gray, Mathews, and MacRobert, *A Treatise onBessel Functions and Their Applications to Physics* (The Macmillan Company, London, 1922).

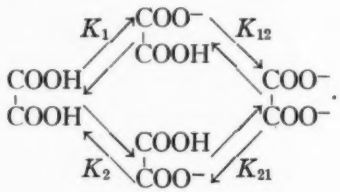
TABLE II.

	ΔpK		D_E				U_0			
			$V_0=3000$		$V_0=2000$		$V_0=3000$		$V_0=2000$	
	H_2O	60% alc.	H_2O	60% alc.	H_2O	60% alc.	H_2O	60% alc.	H_2O	60% alc.
Ethylene diamine	3.02	3.30	31.9	28.4	32.0	28.5	1180	1330	1180	1320
Oxalic acid	2.97	3.51	33.7	27.5	33.8	27.6	81	99	80	99
Glycine	1.99		39.4		39.4		−89		−89	
α-Alanine	1.92		40.8		40.8		−86		−86	
Leucine	2.01		39.0		39.0		−90		−90	
α-Amino butyric acid	1.89		41.5		41.5		−85		−85	

III. CALCULATIONS

Oxalic Acid

We consider the well-known microscopic equilibria[11,12] for oxalic acid:



The ordinary gross dissociation constants are $K_{(1)}$ and $K_{(2)}$. Then

$$K_1=K_2;\quad K_{(1)}=2K_1;$$
$$K_{12}=K_{21};\quad K_{(2)}=K_{12}/2. \tag{13}$$

$U=0$ for all species except the oxalate ion. Then, by Eq. (6),

$$K_{12}=K_{12}^0\int_0^{2\pi}e^{-(U+V)/RT}d\theta\Big/\int_0^{2\pi}e^{-V/RT}d\theta. \tag{14}$$

Using Eqs. (9), (10), and (13), Table I, and the fact that $K_{12}^0=K_1$, Eq. (14) becomes

$$\Delta pK=pK_{(2)}-pK_{(1)}=\frac{m}{4.606}-\log I_0\left(\frac{u}{2}+\frac{v}{2}\right)+\log I_0\left(\frac{v}{2}\right)+\log 4$$
$$=\frac{80.9}{D_E}-\log I_0\left(\frac{2.33}{D_E}+\frac{v}{2}\right)+\log I_0\left(\frac{v}{2}\right)+0.60. \tag{15}$$

Since ΔpK is known experimentally, D_E may easily be calculated by successive approximations (the functions $I_n(a)$ are available in tables[10]) for a given value of V_0. The results of such calculations are given in Table II for $V_0=2000$ and 3000 cal./mole, and for water and 60 percent alcohol (by volume) as solvents. U_0 (Table II) is obtained from D_E and Table I.

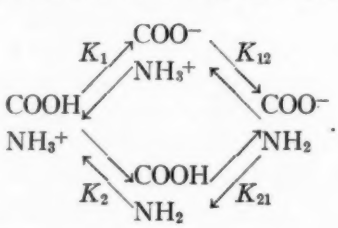
Ethylene Diamine

Corresponding to Eq. (15) [see Eq. (11)],

$$\Delta pK=\frac{81.0}{D_E}+\log I_0\left(\frac{v}{2}\right)+0.60-\log\left[I_0\left(\frac{32.3}{D_E}\right)I_0\left(\frac{v}{2}\right)+2I_3\left(\frac{32.3}{D_E}\right)I_1\left(\frac{v}{2}\right)+\cdots\right]. \tag{16}$$

α-Amino Acids

We shall consider four related α-amino acids and take the same structural parameters for each. The notation to be used is as follows:



For these amino acids we may write $K_{(1)}=K_1$ and $K_{(2)}=K_{12}$. Also, we make an approximation:[7] $K_2=K_E$, where K_E is the dissociation constant of the ester $NH_3^+-CHR-COOC_2H_5$. Now $K_{12}^0=K_2$, so that

$$K_{(2)}=K_E\int_0^{2\pi}e^{-V/RT}d\theta\Big/\int_0^{2\pi}e^{-(U+V)/RT}d\theta, \tag{17}$$

[11] E. Q. Adams, J. Am. Chem. Soc. **38**, 1503 (1916).
[12] See also, for example, T. L. Hill, J. Am. Chem. Soc. (in press).

TABLE III.

Dithionic acid and ions	U_0, cal./mole $D_E=30$	Other corresponding structures
$(O_3S-SO_3)^-(A_{123456})$	126	$(O_3P-PO_3)^{=}$
$[O_3S-SO_2(OH)]^-(A_{12346})$	84	$[O_3P-PO_2(OH)]^{=}$, $(O_3S-SO_2)^-$
$O_3S-SO(OH)_2(A_{1234})$	42	$[O_3P-PO(OH)_2]^-$, $[O_3S-SO(OH)]^-$
$(HO)O_2S-SO_2(OH)(A_{1245})$	1000	$[(HO)O_2P-PO_2(OH)]^-$, $[(HO)O_2S-SO_2]^-$, $(O_2S-SO_2)^-$
$[(HO)O_2S-SO(OH)_2]^+(A_{124})$	920	$[(HO)O_2P-PO(OH)_2]^-$, $(HO)O_2S-SO(OH)$, $(HO)_2OS-SO_2$, $[O_2S-SO(OH)]^-$
$[(HO)_2OS-SO(OH)_2]^{++}(A_{14})$	960	$(HO)_2OP-PO(OH)_2$, $[(HO)_2OS-SO(OH)]^+$, $(HO)OS-SO(OH)$

where U is the electrostatic potential energy function of the dipolar ion (Table I). One obtains from Eq. (11),

$$\Delta pK = pK_{(2)} - pK_E = \frac{78.4}{D_E} - \log I_0\left(\frac{v}{2}\right) + \log\left[I_0\left(\frac{2.97}{D_E}\right)I_0\left(\frac{v}{2}\right) - 2I_3\left(\frac{2.97}{D_E}\right)I_1\left(\frac{v}{2}\right) + \cdots\right]. \quad (18)$$

This reduces, within the limits of experimental error, to $D_E = 78.4/\Delta pK$.

Dithionic Acid

On the basis of (1) the results in Table II, (2) calculations for spherical inorganic oxygen acids[13] and (3) preliminary calculations for pyrophosphoric acid, we assume $D_E = 30$ for dithionic acid and its ions.

Using $D_E = 30$, the values of U_0 in Table I may now be converted into units of cal./mole. These are given in Table III, together with related structures of a few other inorganic acids which would be expected to have electrostatic potential energies of the same order of magnitude. Dithionic acid and the positive ions of dithionic acid listed in the table are, of course, virtually completely ionized in water, but they are included for completeness.

As implied above, a variety of microscopically different[12] ionic species must be taken into account in setting up the equilibrium relationships for dithionic acid. We shall write c_{125}, say, for the concentration or activity of the species (A_{125}) with protons dissociated from positions 1, 2, and 5 only, etc. The subscripts of c are written in increasing order. For dissociation constants we use the notation exemplified by the equations

$$K_{125} = \frac{c_{125}x}{c_{12}}, \quad K_{152} = \frac{c_{125}x}{c_{15}}, \quad K_{251} = \frac{c_{125}x}{c_{25}}$$

(all subscripts of K other than the last one are written in increasing order). These are equilibrium constants for the dissociation of protons 5, 2, and 1, respectively, from A_{12}, A_{15}, and A_{25}, respectively, to form, in all cases, A_{125}. It proves possible to include all microscopic ions in the discussion, employing only those equilibrium constants in which *all* subscripts occur in increasing order.

Looking along the S–S bond of dithionic acid, there are 120° angles between oxygen atoms and the two SO_3-groups are structurally identical. For acids in which this type of symmetry exists, a study[12] of the statistical factors involved leads to the following relations between successive gross dissociation constants and microscopic dissociation constants:

$$K_{(1)} = 6K_1, \quad K_{(2)} = \frac{2K_{12}+3K_{14}}{2},$$

$$K_{(3)} = \frac{2K_{12}K_{123}+9K_{12}K_{124}+9K_{14}K_{145}}{3(2K_{12}+3K_{14})},$$

$$K_{(4)} = \frac{3(K_{12}K_{123}K_{1234}+K_{14}K_{145}K_{1456}+3K_{12}K_{124}K_{1245})}{2K_{12}K_{123}+9K_{12}K_{124}+9K_{14}K_{145}}, \quad (19)$$

$$K_{(5)} = \frac{K_{12}K_{123}K_{1234}K_{12345}+K_{12}K_{124}K_{1245}K_{12456}}{K_{12}K_{123}K_{1234}+K_{14}K_{145}K_{1456}+3K_{12}K_{124}K_{1245}},$$

$$K_{(6)} = \frac{K_{12}K_{123}K_{1234}K_{12345}K_{123456}}{3(K_{12}K_{123}K_{1234}K_{12345}+K_{12}K_{124}K_{1245}K_{12456})}.$$

[13] T. L. Hill, J. Am. Chem. Soc. 65, 1564 (1943). Using the experimental dissociation constants and distances between negatively charged oxygen atoms, one finds that D_E, for the nine acids discussed, falls between 18 and 23, with one exception (16). These results check at least qualitatively with the equations of Kirkwood and Westheimer (reference 2).

TABLE IV.

Structure	$u/2$	$e^{-m/2}$	σ $V_0=3000$	σ $V_0=2000$	S $V_0=2000$
A_{14}	0.811	5.06×10^{-3}	1.188	1.184	6.00×10^{-3}
A_{124}	0.776	3.35×10^{-5}	1.145	1.151	3.86×10^{-5}
A_{1234}	0.0355	1.68×10^{-7}	1.027	1.022	1.72×10^{-7}
A_{1245}	0.845	8.32×10^{-10}	1.210	1.205	1.00×10^{-9}
A_{12345}	0.0710	3.16×10^{-14}	1.053	1.049	3.32×10^{-14}
A_{123456}	0.106	5.13×10^{-21}	1.089	1.077	5.52×10^{-21}

Define

$$S_{r_1r_2\cdots}=\frac{\int_0^{2\pi}\exp\{-[(U'_{r_1r_2\cdots}+V)]/RT\}d\theta}{\int_0^{2\pi}e^{-V/RT}d\theta} \tag{20}$$

$$=\exp(-m_{r_1r_2\cdots}/2)\sigma_{r_1r_2\cdots} \tag{21}$$

having factored $\exp(-m_{r_1r_2\cdots}/2)$ out of the definite integral in the numerator. Then, noting that

$$S_{124}=S_{145},\quad S_{1234}=S_{1456},\quad S_{12345}=S_{12456},$$

we have, from Eq. (6),

$$\begin{aligned}
&K_{12}=K_1\omega,\quad K_{14}=K_1S_{14},\quad K_{123}=K_1\omega^2,\\
&K_{124}=K_1S_{124},\quad K_{145}=K_1\omega S_{124}/S_{14},\\
&K_{1234}=K_1S_{1234},\quad K_{1456}=K_1\omega^2S_{1234}/S_{124},\\
&K_{1245}=K_1\omega S_{1245}/S_{124},\\
&K_{12345}=K_1\omega S_{12345}/S_{1234},\\
&K_{12456}=K_1\omega^2S_{12345}/S_{1245},\\
&K_{123456}=K_1\omega^2S_{123456}/S_{12345},
\end{aligned} \tag{22}$$

where ω is a constant electrostatic factor (related to $U-U'$):

$$\omega=\exp(-N\epsilon^2/D_Er_1RT),$$

r being the distance between two oxygen atoms bonded to the same sulphur atom. On substituting Eqs. (22) into Eqs. (19), we arrive finally at

$$\begin{aligned}
&K_{(1)}=6K_1,\quad K_{(2)}=\frac{K_1(2\omega+3S_{14})}{2},\\
&K_{(3)}=\frac{2K_1\omega(\omega^2+9S_{124})}{3(2\omega+3S_{14})},\\
&K_{(4)}=\frac{3K_1\omega(2\omega S_{1234}+3S_{1245}),}{2(\omega^2+9S_{124})},\\
&K_{(5)}=\frac{2K_1\omega^2S_{12345}}{2\omega S_{1234}+3S_{1245}},\quad K_{(6)}=\frac{K_1\omega^2S_{123456}}{6S_{12345}}.
\end{aligned} \tag{23}$$

TABLE V.

ω	$K_{(5)}/K_{(6)}$	$K_{(5)}/K_{(6)}$ K and H*	c_{14}/c_{12}	c_{1245}/c_{1234}
4.90×10^{-4}	7.56×10^{2}	1.6×10^{3}	12.2	11.9

* Kossiakoff and Harker, reference 4 of text.

The corresponding treatment for an acid with four instead of six potential OH groups (e.g., hyposulphurous acid), leads to

$$\begin{aligned}
&K_{(1)}=4K_1,\quad K_{(2)}=\frac{K_{12}+2K_{13}}{2},\\
&K_{(3)}=\frac{K_{12}K_{123}+K_{13}K_{134}}{K_{12}+2K_{13}},\\
&K_{(4)}=\frac{K_{12}K_{123}K_{1234}}{2(K_{12}K_{123}+K_{13}K_{134})},
\end{aligned} \tag{24}$$

and

$$\begin{aligned}
&K_{(1)}=4K_1,\quad K_{(2)}=\frac{K_1(\omega+2S_{13})}{2},\\
&K_{(3)}=\frac{2K_1\omega S_{123}}{\omega+2S_{13}},\quad K_{(4)}=\frac{K_1\omega S_{1234}}{4S_{123}},
\end{aligned} \tag{25}$$

provided that the two AO_2 groups are structurally identical. The O−A−O bond angle may have any value.

The calculations of $S_{r_1r_2\cdots}$ for dithionic acid are summarized in Table IV [having used especially Eqs. (6), (10), (11), and (12)]. It will be observed that σ is the (electrostatic) hindered-rotational factor and approaches unity for several of the ions.

Employing Eqs. (23), the values of $S_{r_1r_2\cdots}$ in Table IV have been used with the constant electrostatic factor ω to evaluate $K_{(5)}/K_{(6)}$ for dithionic acid (these constants are, of course, ordinarily numbered K_1/K_2). The result is given in Table V and compared with the theoretical value of Kossiakoff and Harker[4] (based on a rigid model, S−S=2.01A and a curve for the dielectric constant in the neighborhood of a charge). The two values would agree for a D_E of about 27.

Finally, we make use of the above results to calculate the concentration ratio between two ions with the same net charge but with different

charge distributions. We employ[12]

$$\frac{c_{r_1r_2\cdots r_k}}{c_{s_1s_2\cdots s_k}}=\frac{K_{r_1}K_{r_1r_2}\cdots K_{r_1r_2\cdots r_k}}{K_{s_1}K_{s_1s_2}\cdots K_{s_1s_2\cdots s_k}}$$

and the previous values of $S_{r_1r_2\cdots}$ and ω for dithionic acid. The results, for two examples, are presented in the last two columns of Table V. The concentrations of the symmetrical ions are highly favored in the equilibria, as expected.

IV. DISCUSSION

In this paper, the principal concern is the calculation of the electrostatic potential barriers for the examples chosen. A consideration of the effective dielectric constants will be reserved until a later time. However, it may be remarked that the effect of a change of solvent on D_E and therefore on U_0 is as expected.

There are two orders of magnitude of U_0 in Tables II and III. Those values in the region from approximately 40 to 130 cal./mole are practically negligible compared to other contributions to hindered rotation. The second group of U_0 values falls in the range from approximately 900 to 1300 cal./mole. These are certainly significant, though they are still probably not the principal contribution to the total potential energy.

As has been seen, the actual electrostatic potential barriers calculated from dissociation constants (Table II) are almost independent of the choice of V_0, so that it has not seemed worth while here to attempt to make more specific assignments—which would necessarily be somewhat uncertain—of V_0 in particular cases. Because of this situation, detailed calculations of root mean square interatomic distances have not been carried out ($U'+V$ is involved in the integrations and hence the selection of V_0 is important). However, inasmuch as V_0 will generally be of the order of magnitude of several kilocalories per mole, the interatomic distances will be approximately those of the particular configuration (or an average—weighted, if necessary—over the finite number of configurations) possessing minimum total potential energy (neglecting the electrostatic effect, "staggered" rather than "lined up" arrangements are most stable). The same would be true of the dipole moments of more complicated dipolar ions than those considered here (since—due to resonance—the "center of gravity" of the negative charge of the carboxylate group is on the extension of the C−C bond, the dipole moments of the present amino acids are independent of θ). For example, let us consider briefly β-alanine and take the same bond angles and distances as for glycine, with the addition of a tetrahedral C−C−C angle. For the purpose of calculating the dipole moment, the negative charge in the dipolar ion is located 2.12A from the α-carbon atom on the extension of the $C_\alpha-C_{COOH}$ bond. We assume the center of positive charge to be on the nitrogen atom. Let θ be the angle between the $C_\beta-N$ bond and the $C_\alpha-C_{COOH}$ bond, looking along the $C_\alpha-C_\beta$ bond. Then, if the dipole distance is d,

$$d^2=13.37-5.23\cos\theta\ (\text{in A}^2)$$

from which

$$d_{max}=4.31\text{A},\quad d_{min}=2.85\text{A},\quad (\bar{d}^2)^{\frac{1}{2}}_{\substack{\text{free}\\\text{rot}}}=3.66\text{A}.$$

The potential function hindering rotation is approximately $V(\theta)=\text{const.}+\frac{1}{2}V_0\cos 3\theta$, where V_0 is probably in the neighborhood of 3.4 kcal./mole (as in propane). The electrostatic potential energy is no doubt quite small compared to this value, and we ignore it. On this basis we find

$$(\bar{d}^2)^{\frac{1}{2}}_{V(\theta)}=(\bar{d}^2)^{\frac{1}{2}}_{\substack{3\text{ min}\\\text{positions}}}=(\bar{d}^2)^{\frac{1}{2}}_{\substack{\text{free}\\\text{rot}}}=3.66\text{A},$$

$$(\bar{d})_{\substack{3\text{ min}\\\text{positions}}}=3.62\text{A},$$

so that for this case the free rotational value, the integrated value using $V(\theta)$ and the average over the three minimum energy configurations only, all give the same result for $\bar{d}^2$.

In order to account for experimental results, freedom of rotation has been postulated in dipolar ions.[14] It would appear, however, that free rotation is a sufficient condition but not a necessary one[15] for this purpose. Hindered rotation of the type mentioned above for β-alanine seems a good deal more likely, and would likewise fit the experimental observations.[16]

Note added in proof: See the note added in proof to part II of this series.

[14] J. Wyman, J. Phys. Chem. **43**, 143 (1939).
[15] See footnote 8 in reference 2.
[16] See the discussion by Edsall on pp. 152–154 of reference 7.

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The Electrostatic Contribution to Hindered Rotation in Certain Ions and Dipolar Ions in Solution. II

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The previous treatment of ethylene diamine, oxalic acid, glycine, α-alanine, leucine, α-amino butyric acid, and dithionic acid is extended here to analogous compounds with one additional angle of rotation: 1,3-propane diamine, malonic acid, β-alanine, and pyrophosphoric acid.

I. INTRODUCTION

WE continue here a consideration of the electrostatic contribution to restricted rotation and its influence on electrolytic equilibria. In an earlier paper[1] a general procedure was outlined, and applied to several examples in which only one rotational angle entered into the specification of the relative positions of the charges in the molecule or ion. In the present communication, corresponding examples, with two rotational angles, are treated. The previous notation and equations will be used as much as possible to avoid repetition.

If we are examining the equilibrium

$$A_a \rightleftarrows A_i + H^+$$

for which the thermodynamic dissociation constant is K, we have by Eq. I (6)[2]

$$K = K^0 \frac{\int_0^{2\pi}\int_0^{2\pi} \exp\{-[U^i(\theta,\theta')+V(\theta,\theta')]/RT\}d\theta d\theta'}{\int_0^{2\pi}\int_0^{2\pi} \exp\{-[U^a(\theta,\theta')+V(\theta,\theta')]/RT\}d\theta d\theta'}, \quad (1)$$

where U^a and U^i are electrostatic potential energies of interaction between non-permanent[1] charges in A_a and A_i, respectively; V is the potential energy function representing inhibited rotation about θ and θ' arising from other sources; K^0 is the value of K that would obtain in the absence of interactions between non-permanent charges in A_a and A_i; θ and θ' are angles of rotation about bonds.

The substances to be discussed here are 1,3-propane diamine, β-alanine, malonic acid, and pyrophosphoric acid. We assume, as before, that the positive charges on the 1,3-propane diammonium ion and on the dipolar ion of β-alanine are point charges on the nitrogen atoms, and that one-half an electronic charge resides on each oxygen atom of a carboxylate group. Also, in the pyrophosphate ion we assume a formal charge distribution;[3,4] that is, a negative charge on each of the six peripheral oxygen atoms and a positive charge on each phosphorus atom. The bond angles and distances used for the organic compounds are the same as for the corresponding compounds in reference 1. For pyrophosphoric acid and its ions:[5] P−O (central) distance, 1.56A; P−O (peripheral) distance, 1.52A; P−O−P angle, 152°; all other angles tetrahedral.

Calculations and dissociation constant data for β-alanine[6] and pyrophosphoric acid[3] are for 25°C; those for malonic acid[7] and 1,3-propane diamine[7] are for 20°C.

II. POTENTIAL FUNCTIONS

It is again found that the calculated value of D_E, the effective dielectric constant [the only

[1] T. L. Hill, J. Chem. Phys. **11**, 545 (1943).
[2] Equation (6), part I (reference 1).
[3] A. Kossiakoff and D. Harker, J. Am. Chem. Soc. **60**, 2047 (1938).
[4] G. E. Branch and M. Calvin, *The Theory of Organic Chemistry* (Prentice-Hall, Inc., New York, 1941).
[5] G. R. Levi and G. Peyronel, Zeits. f. Krist. **92**, 190 (1935).
[6] E. J. Cohn and J. T. Edsall, *Proteins, Amino Acids, and Peptides as Ions and Dipolar Ions* (Reinhold Publishing Corporation, New York, 1943).
[7] G. Schwarzenbach, Helv. Chim. Acta **16**, 522 (1933).

TABLE I.

1,3-Propane diamine	$U'/RT=A+B\cos\theta'+(C+D\cos\theta')\cos(\theta-\alpha\sin\theta')$ $V=\text{const.}+\frac{V_0}{2}(\cos 3\theta+\cos 3\theta')$
β-Alanine	$U'/RT=A+B\cos\theta'+(C+D\cos\theta')\cos(2\theta-\alpha\sin\theta')$ $V=\text{const.}+\frac{V_0}{2}\cos 6\theta+\frac{V_0'}{2}\cos 3\theta'$
Malonic acid	$U'/RT=A+B\cos 2\theta'+(C+D\cos 2\theta')\cos(2\theta-\alpha\sin 2\theta')$ $V=\text{const.}+\frac{V_0}{2}(\cos 6\theta+\cos 6\theta')$
Pyrophosphoric acid, A_{14}	$U'/RT=A+B\cos\theta'+(C+D\cos\theta')\cos(\theta-\theta')$ $V=\text{const.}+\frac{V_0}{2}(\cos 3\theta+\cos 3\theta')$
A_{124}	$U'/RT=A+B\cos\left(\theta'+\frac{\pi}{3}\right)+\left[C+D\cos\left(\theta'+\frac{\pi}{3}\right)\right]\cos\left[\theta-\alpha\sin\left(\theta'+\frac{\pi}{3}\right)\right]$
A_{1234}	$U'/RT=A+B\cos 3\theta'+(C+D\cos 3\theta')\cos(\theta-\alpha\sin 3\theta')$
A_{1245}	$U'/RT=A+B\cos\left(\theta'+\frac{\pi}{3}\right)+\left[C+D\cos\left(\theta'+\frac{\pi}{3}\right)\right]\cos\left[\theta-\alpha\sin\left(\theta'+\frac{\pi}{3}\right)+\frac{\pi}{3}\right]$
A_{12345}	$U'/RT=A+B\cos 3\left(\theta'+\frac{\pi}{3}\right)+\left[C+D\cos 3\left(\theta'+\frac{\pi}{3}\right)\right]\cos\left(\theta-\alpha\sin 3\theta'+\frac{\pi}{3}\right)$
A_{123456}	$U'/RT=A+B\cos 3\theta'+(C+D\cos 3\theta')\cos 3(\theta-\theta')$

V is the same for all species of pyrophosphoric acid.

unknown parameter in Eq. (1)], is quite insensitive to V_0, the potential barrier corresponding to V. We take, more or less arbitrarily, $V_0=1000$ cal./mole [it is not necessary actually to use this value—see Eq. (15)] for the rotation of a carboxyl group about the adjacent C−C bond and $V_0=3400$ cal./mole for the rotation of a methylamine group about the adjacent C−C bond. We make the approximation, as was done tacitly before, that the function V has equal maxima and equal minima. For pyrophosphoric acid we shall merely neglect V, inasmuch as the extent of dependence of D_E on V is quite trivial compared to other uncertainties which arise in this more complicated case. Moreover, V_0 should probably be rather small.

The form of V for the various substances is shown in Table I. A_{14} is the species of pyrophosphoric acid in which protons have been dissociated from positions 1 and 4 only, etc.; the numbering corresponds to that in reference 1. That is, looking out from the central oxygen atom, the three oxygen atoms bonded to one phosphorus atom are numbered 1, 2, and 3 in a counterclockwise direction (θ' increases); looking toward the other phosphorus atom, the remaining oxygen atoms are numbered 4, 5, and 6 in a clockwise direction (θ increases). $\theta=\theta'=0$ for the distance of nearest approach between positions 1 and 4 (thus, in this configuration, position 2 is at $\theta'=120°$, position 3 at $\theta'=240°$, position 5 at $\theta=120°$, and position 6 at $\theta=240°$).

The functions U are obtained by calculating the reciprocal of the interatomic distance r, from

$$r^2=a_1+a_2\cos\theta+a_3\cos\theta'+a_4\cos\theta\cos\theta'+a_5\sin\theta\sin\theta' \quad (2)$$

for adequate intervals of θ and θ'. Values of a_1, a_2, a_3, a_4, and a_5 are given in Table II, calculated from the bond angles and distances. The angle θ is related to the rotation of the carboxylate group in β-alanine, θ' to that of the methylamine group.

All final functions (U), except for 1,3-propane

TABLE II.

	a_1	a_2	a_3	a_4	a_5	A	B	C	D
1,3-Propane diamine	14.83	−5.09	−5.09	−1.14	−3.42	0.310	0.0823	0.0823	0.0595
β-Alanine	14.55	−4.29	−5.22	−0.96	−2.88	−.289	−.0634	−.0134	−.0122
Malonic acid	14.48	−4.43	−4.43	−0.81	−2.43	.278	.00865	.00865	.0051
Pyrophosphoric acid, A_{14}	20.20	−2.77	−2.77	−3.61	−4.09	.231	.0220	.0259	.0220
A_{124}						.451	.0205	.0339	.0243
A_{1234}						.682	.00155	.0559	.0016
A_{1245}						.903	.0348	.0348	.0248
A_{12345}						1.354	.00095	.0553	.00055
A_{123456}						2.036	.0006	.00215	.0006

a's in units of A^2; A, B, C, and D in units of A^{-1}.

diamine and A_{14}, are obtained in the usual manner by addition of component parts. U may be represented approximately by the expressions given in Table I. $U'=U$ except for some species of pyrophosphoric acid; for these, U' is that part of U exclusive of interactions between charged oxygen atoms bonded to the same phosphorus atom [these are taken into account by the factor ω, introduced in Eq. (17)].

The constants A, B, C, and D are calculated as follows: Let $U'_{\max}(\theta')$ be the maximum value of U' (as θ varies from 0 to 2π) for a fixed angle θ'; similarly for $U'_{\min}(\theta')$. Then we write

$$M'(\theta')=U'_{\max}(\theta')+U'_{\min}(\theta'),$$
$$U_0'(\theta')=|U'_{\max}(\theta')|-|U'_{\min}(\theta')|. \tag{3}$$

Now let $M'_{\max}$ be the maximum value of $M'(\theta')$, as θ' varies from 0 to 2π; similarly for $M'_{\min}$, $U'_{0\max}$ and $U'_{0\min}$. Define

$$A=\frac{M'_{\max}+M'_{\min}}{4RT},\qquad B=\frac{|M'_{\max}|-|M'_{\min}|}{4RT},$$
$$C=\frac{U'_{0\max}+U'_{0\min}}{4RT},\qquad D=\frac{|U'_{0\max}|-|U'_{0\min}|}{4RT}. \tag{4}$$

These constants have been calculated in units of A^{-1} and are presented in Table II. The values given there must be multiplied by $N\epsilon^2/D_ERT$ in order to be used in Table I.

III. CALCULATIONS

1,3-Propane Diamine

From Eq. I (14) and Table I,

$$\Delta pK=\frac{A}{2.303}-\log\sigma'+\log 4$$
$$=\frac{76.6}{D_E}-\log\sigma'+0.60, \tag{5}$$

$$\sigma'=\frac{\int_0^{2\pi}\int_0^{2\pi}\exp\left[-B\cos\theta'-(C+D\cos\theta')\cos(\theta-\alpha\sin\theta')-\frac{v}{2}(\cos 3\theta+\cos 3\theta')\right]d\theta d\theta'}{\int_0^{2\pi}\int_0^{2\pi}\exp\left[-\frac{v}{2}(\cos 3\theta+\cos 3\theta')\right]d\theta d\theta'}, \tag{6}$$

in which $v/2=V_0/2RT$. The constant α may be evaluated from Eq. (2). One finds

$$\alpha=\tan^{-1}[a_5/(a_2^2-a_4^2)^{\frac{1}{2}}].$$

Now

$$\int_0^{2\pi}\int_0^{2\pi}\exp\left[-\frac{v}{2}(\cos 3\theta+\cos 3\theta')\right]d\theta d\theta'$$
$$=4\pi^2I_0^2\left(\frac{v}{2}\right), \tag{7}$$

where $I_n(x)$ is a modified Bessel function of the first kind. There remains the evaluation of the definite integral in the numerator of Eq. (6). This may be done by making use of the following expansions:[8]

$$e^{-a\cos n\theta}=I_0(a)+2\sum_{s=1}^{\infty}(-1)^sI_s(a)\cos sn\theta, \tag{8}$$

[8] Gray, Mathews, and MacRobert, *A Treatise on Bessel Functions and Their Applications to Physics* (The Macmillan Company, London, 1922).

TABLE III.

	ΔpK		D_E		σ'		CRT, cal./mole		W_0, cal./mole	
	H_2O	60% alc.	H_2O	60% alc.	H_2O	60% alc.	H_2O	60% alc.	H_2O	60% alc.
1,3-Propane diamine	2.04	2.24	47.3 (47.6)	40.9 (41.4)	1.51 (1.48)	1.70 (1.64)	577 (574)	667 (660)	2310 (2290)	2670 (2640)
β-Alanine	1.06		68.3		1.07		−65		746	
Malonic acid	2.87	3.99	30.1	20.2	1.01	1.03	95	142	382	568

( ) values are for $V_0=0$. Values for β-alanine and malonic acid are unchanged on setting $V_0=0$.

$$I_n(a+b)=\sum_{s=0}^{n} I_s(a)I_{n-s}(b)+\sum_{s=1}^{\infty}\{I_s(a)I_{n+s}(b)+I_{n+s}(a)I_s(b)\}, \quad (9)$$

$$I_n(a)=\sum_{s=0}^{\infty}\frac{(a/2)^{2s+n}}{s!(s+n)!}, \quad (10)$$

$$\cos(a\sin\theta)=J_0(a)+2J_2(a)\cos 2\theta+2J_4(a)\cos 4\theta+\cdots,$$

where $J_n(a)$ is a Bessel function of the first kind.

We have, from Eqs. (6), (7), and (8),

$$4\pi^2 I_0^2\left(\frac{v}{2}\right)\sigma'=2\pi\left\{I_0\left(\frac{v}{2}\right)\int_0^{2\pi}\exp\left(-B\cos\theta'-\frac{v}{2}\cos 3\theta'\right)I_0(C+D\cos\theta')d\theta'+2\sum_{p=1}^{\infty}I_p\left(\frac{v}{2}\right)\int_0^{2\pi}\exp\left(-B\cos\theta'-\frac{v}{2}\cos 3\theta'\right)I_{3p}(C+D\cos\theta')\cos(3p\alpha\sin\theta')d\theta'\right\}. \quad (11)$$

Only the first integral need be given here (neglecting higher ones introduces an error of approximately 0.2 percent). To this degree of accuracy,

$$\sigma'=(D_0E_0+D_1E_1+D_2E_2+D_3E_3)\Big/I_0\left(\frac{v}{2}\right) \quad (12)$$

$$\left.\begin{aligned} D_0&=I_0(C) & D_1&=DI_1(C)\\ D_2&=\frac{D^2}{4}[I_0(C)+I_2(C)] & D_3&=\frac{D^3}{8}I_1(C)\end{aligned}\right\}$$

$$\left.\begin{aligned} E_0&=I_0(B)I_0\left(\frac{v}{2}\right)+2I_3(B)I_1\left(\frac{v}{2}\right)\\ -E_1&=I_1(B)I_0\left(\frac{v}{2}\right)+I_2(B)I_1\left(\frac{v}{2}\right)\\ E_2&=\tfrac{1}{2}[I_0(B)+I_2(B)]I_0\left(\frac{v}{2}\right)+\tfrac{1}{2}[I_1(B)+2I_3(B)]I_1\left(\frac{v}{2}\right)\\ -E_3&=\tfrac{1}{4}[3I_1(B)+I_3(B)]I_0\left(\frac{v}{2}\right)+\tfrac{1}{4}[I_0(B)+3I_2(B)]I_1\left(\frac{v}{2}\right)+\tfrac{1}{4}I_3(B)I_2\left(\frac{v}{2}\right).\end{aligned}\right\}$$

Using the experimental value of ΔpK and $v/2=3400/2RT=2.92$, Eq. (5) may now be solved for D_E by successive approximations. The results are given in Table III. The values in parentheses are those found when we neglect V (set $v/2=0$). In this case, Eq. (12) becomes

$$\sigma'=I_0(C)I_0(B)-DI_1(C)I_1(B)+\frac{D^2}{8}[I_0(C)+I_2(C)][I_0(B)+I_2(B)]-\frac{D^3}{32}I_1(C)[3I_1(B)+I_3(B)]. \quad (13)$$

Employing Eq. (13) rather than Eq. (12) would result in an error in D_E of roughly only one percent. This serves to illustrate further the relative insensitiveness of D_E to V_0. Furthermore, as is apparent from the effective dielectric constants and the values of B, C, and D in Table II, this error for 1,3-propane diamine would be greater than the analogous error for any other molecule or species considered in this paper.

The electrostatic potential barrier here is not a constant but is a function of θ': $RT(C+D\cos\theta')$. The average value, however, is CRT and this quantity is included in Table III.

TABLE IV. Pyrophosphoric acid.

ω	$D_E=20$, 1.20×10^{-5} FR	$D_E=20$, 1.20×10^{-5} HR	$D_E=25$, 1.16×10^{-4} FR	$D_E=30$, 5.25×10^{-4} FR	$D_E=30$, 5.25×10^{-4} HR	K and H[2]	Obs.[3]
$\Delta pK_{(3)-(5)}$	3.42	3.40	2.87	2.47	2.46	2.3	1.1
$\Delta pK_{(3)-(6)}$	4.78	4.78	3.76	3.15	3.15	3.8	4.7
$\Delta pK_{(4)-(5)}$	3.40	3.67	2.88	2.48	2.61	2.7	2.7
c_{14}/c_{12}	131.	162.	49.0	25.7	28.6		

FR = Free rotation; HR = Hindered rotation.

TABLE V. Pyrophosphoric acid.

	e^{-A}	σ'	S	CRT, cal./mole	W_0 cal./mole
A_{14}	1.35×10^{-2}	1.11	1.50×10^{-2}	286	1130
A_{124}	2.22×10^{-4}	1.14	2.54×10^{-4}	375	1290
A_{1234}	2.98×10^{-6}	1.29	3.84×10^{-6}	619	1270
A_{1245}	4.73×10^{-8}	1.21	5.72×10^{-8}	385	1620
A_{12345}	1.07×10^{-11}	1.28	1.37×10^{-11}	612	1240
A_{123456}	3.16×10^{-17}	1.00	3.16×10^{-17}	24	61

$D_E=30$.

The quantity W_0, in Table III, is defined by $W_0=U'_{\max}-U'_{\min}$, where $U'_{\max}$ and $U'_{\min}$ are the maximum and minimum values, respectively, of $U'(\theta,\theta')$, over all possible angles θ and θ'. W_0 thus indicates the range in U'.

β-Alanine

Corresponding to Eq. I (18), we have, from Table II,

$$\Delta pK=pK_{(2)}-pK_E=\frac{70.4}{D_E}+\log\sigma', \qquad (14)$$

where $K_{(2)}$ is the second acidic dissociation constant of β-alanine and K_E is the acidic dissociation constant of the ethyl ester. The integration of the functions in Table I leads, to the desired degree of accuracy, to

$$\sigma'=I_0(C)I_0(B), \qquad (15)$$

which is the leading term in Eq. (13) [and Eq. (12)]. Thus, the values of D_E, σ', CRT, and W_0 in Table III are the same for $V_0=1000$ cal./mole and $V_0=0$.

Malonic Acid

Instead of Eq. (5),

$$\Delta pK=\frac{68.6}{D_E}-\log\sigma'+0.60, \qquad (16)$$

where, as for β-alanine, σ' is given by Eq. (15).

Pyrophosphoric Acid

The point of view is somewhat different here. There is a wide variety of different molecular species interrelated by various equilibria. For present purposes we make the rather rough approximation that the same D_E applies in all equilibria for this single acid and its ions.

Let $K_{(1)}$, $K_{(2)}$, etc., be successive dissociation constants of $[(HO)_3POP(OH)_3]^{++}$. The constants $K_{(3)}$, $K_{(4)}$, $K_{(5)}$, and $K_{(6)}$ are known experimentally, though apparently with some uncertainty.[3,4]

The procedure is to find that value of D_E which best fits the experimental values of $K_{(3)}/K_{(4)}$, $K_{(4)}/K_{(5)}$, and $K_{(5)}/K_{(6)}$. The same microscopic equilibrium relationships hold here as for dithionic acid,[1] so we may use Eqs. I (23):

$$K_{(1)}=6K_1, \quad K_{(2)}=\frac{K_1(2\omega+3S_{14})}{2},$$

$$K_{(3)}=\frac{2K_1\omega(\omega^2+9S_{124})}{3(2\omega+3S_{14})},$$

$$K_{(4)}=\frac{3K_1\omega(2\omega S_{1234}+3S_{1245})}{2(\omega^2+9S_{124})},$$

$$K_{(5)}=\frac{2K_1\omega^2S_{12345}}{2\omega S_{1234}+3S_{1245}}, \quad K_{(6)}=\frac{K_1\omega^2S_{123456}}{6S_{12345}}, \qquad (17)$$

in which

$$S_{r_1r_2\cdots}=\exp(-A_{r_1r_2\cdots})\sigma'_{r_1r_2\cdots},$$

$$\omega=\exp(-N\epsilon^2/D_Er'RT),$$

and K_1 is the equilibrium constant for the dissociation of a particular proton from $H_6P_2O_7^{++}$. The electrostatic factor ω is a constant, inasmuch as r' is the distance between two oxygen atoms bonded to the same phosphorus atom.

Calculations have been made for $D_E=20$ and $D_E=30$. In both cases V has been neglected (its influence on $K_{(3)}/K_{(4)}$, etc., would be relatively insignificant), and Eq. (13) used. Free rotational values ($\sigma'=1$) have also been calculated for D_E equal to 20, 25, and 30. The results obtained are compared with the experimental results and with the theoretical ones of Kossiakoff and Harker[3] in Table IV. It would appear that $D_E=30$ is the best approximate over-all value for pyrophosphoric acid. Details of the calculation for $D_E=30$ are given in Table V.

The above results have been used (Table IV) to calculate the concentration ratio of symmetrical to unsymmetrical pyrophosphoric acid (c_{14}/c_{12}). Other such ratios may of course also be calculated[1] from the data in Table V.

IV. DISCUSSION

As is to be expected, the values of W_0 are generally larger, while those of CRT are smaller, than U_0 for the corresponding compound[1] with but one rotational angle. The conclusion is again that the electrostatic contribution to restricted rotation, for the compounds considered, is in general significantly less important than other contributions, and may be negligible in some cases.

Notwithstanding some uncertainty in the experimental dissociation constants of pyrophosphoric acid, it is fairly clear that the present treatment of this compound (and dithionic acid) is oversimplified and a single D_E is not adequate. It is intended to discuss this question and others relating to the calculated effective dielectric constants in more detail at a later time.

Note added in proof: We have assumed ΔpK to arise from electrostatic and statistical factors only. There is some reason to believe that other factors may be involved to a significant extent in oxalic and malonic acids. Further, it appears possible that the experimental values of ΔpK for ethylene diamine and 1,3-propane diamine are appreciably in error. Calculations for the above four substances may therefore need revision at some later time. However, orders of magnitude would not be changed.

The values of ΔpK mentioned above will be discussed more completely elsewhere.

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The Attainment of Thermal Equilibrium Between a Gas and a Hot Surface*

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IN some experimental determinations of electron affinities[1] of electronegative atoms gas molecules hit a hot filament, the temperature of which is much higher than the temperature at which the dissociation of the gas would be virtually complete. It is necessary in making the calculations to assume that every gas molecule hitting the hot surface is dissociated. This is an extreme case of the general problem of determining to what extent a gas molecule attains thermal equilibrium when it strikes a hot surface —a problem of fundamental concern in heterogeneous catalysis. Consequently it is interesting to note that data from the careful experiments of Bryce[2] can be used to show that, within the limits of experimental error, all the hydrogen molecules hitting a hot tungsten wire come to equilibrium and return to the gas phase as atoms and molecules in equilibrium concentrations determined by the temperature of the wire and the number of molecules striking.

The experimental data consist of several measurements at each of four temperatures of the pressure of hydrogen gas, P_{H_2}, and the volume of hydrogen at N.T.P. dissociated per unit area of filament per second. This volume must be corrected[3] to take into account the fact that only the center of the filament was at the temperature measured. The hydrogen atoms formed were efficiently trapped so that none returned to the filament.

If a filament were in thermal equilibrium with hydrogen gas at the temperature T_S, it would be

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[1] K. J. McCallum and J. E. Mayer, J. Chem. Phys. **11**, 56 (1943).
[2] Bryce, Proc. Camb. Phil. Soc. **32**, 648 (1936).
[3] Langmuir, MacLane, and Blodgett, Phys. Rev. **35**, 478 (1930).

TABLE I.

Temp. °K	log K (calc.)	log K (expt.)
1148	−13.80	−14.09
1243	−12.38	−12.54
1338	−11.18	−11.25
1420	−10.24	−10.30

struck by

$$\frac{P_{\mathrm{H}}\ (\mathrm{eq.})}{N_0(2\pi m_{\mathrm{H}} k T_S)^{\frac{1}{2}}}$$

gram atoms of hydrogen, and by

$$\frac{P_{\mathrm{H_2}}\ (\mathrm{eq.})}{N_0(4\pi m_{\mathrm{H}} k T_S)^{\frac{1}{2}}}$$

moles of hydrogen per cm² per second, where P_{H} (eq.) and $P_{\mathrm{H_2}}$ (eq.) would be the equilibrium pressure of atoms and molecules in the gas. The same numbers of gram atoms and moles must leave the filament under these conditions. The $P_{\mathrm{H_2}}$ (eq.) and P_{H} (eq.) are determined from the known equilibrium constant and the total pressure. The total amount of material hitting the surface is determined by the total pressure.

Now from the value of $P_{\mathrm{H_2}}$ in Bryce's experiment the number of moles of hydrogen hitting unit area of the filament in unit time is calculated, and this is set equal to half the number of moles of atoms plus the number of moles of hydrogen molecules leaving unit area in unit time. Thus:

$$\frac{P_{\mathrm{H_2}}}{N_0(4\pi m_{\mathrm{H}} k T_R)^{\frac{1}{2}}} = \frac{v}{22400} + \frac{P_{\mathrm{H_2}}\ (\mathrm{eq.})}{N_0(4\pi m_{\mathrm{H}} k T_S)^{\frac{1}{2}}},$$

where N_0 is Avogadro's number, v is the corrected volume in cm³, T_S is the surface temperature, and T_R is the temperature of the gas (0°C). From this $P_{\mathrm{H_2}}$ (eq.) may be evaluated. One may calculate P_{H} (eq.) from:

$$\frac{2v}{22400} = \frac{P_{\mathrm{H}}\ (\mathrm{eq.})}{N_0(2\pi m_{\mathrm{H}} k T_S)^{\frac{1}{2}}},$$

the number of gram atoms of hydrogen leaving unit area of surface per unit time. Using these and assuming unit accommodation coefficient,[4] the following expression for the equilibrium constant K_p, for the dissociation of hydrogen, in units of atmospheres, is obtained. The pressure is expressed in microns and the volume in cm³ at N.T.P.

$$K_p = \frac{5.34\times10^{-5} v^2 (T_S)^{\frac{1}{2}}}{P_{\mathrm{H_2}} - 2.66v}.$$

The values for log K calculated from this equation, together with values obtained from data given by Giauque[5] using a value of 102,720[6] calories for the energy of dissociation are listed in Table I. The use of the lowest recorded value of the energy of dissociation for hydrogen (101 kcal.) would give values of log K (expt.) about 0.3 unit less negative in the third column. It is estimated that the error in log K (calc.) due to measurements of pressure and volume is about ±0.02. Uncertainty of temperature (±5°) corresponds to ±0.08 in log K. These inherent errors, together with the fact that the temperature of the gas was probably several degrees higher than the temperature of the outside wall, lead to an estimated precision measure of log K of ±0.2. This precision measure is greater than the difference between the calculated and experimental values for log K except for the lowest temperature where the largest error in temperature measurement is to be expected, as pointed out by Bryce.

Thus it is seen that the equilibrium constant calculated agrees with the known value. In fact, since most reliable values of the energy of dissociation of hydrogen are in the neighborhood of 103 kcal., the calculated equilibrium constant is in error on that side which would mean greater than equilibrium dissociation and hence a contradiction of the second law. Since this is impossible it can only be concluded that within the small experimental error all hydrogen molecules hitting the tungsten filament come to thermal equilibrium with the hot surface.

Naturally, this conclusion cannot be applied in general to gases in contact with hot surfaces. It is known[7] that molecules which are not chemi-

[4] By unit accommodation coefficient it is meant that no molecule striking the surface leaves it before coming to the temperature of the surface.

[5] W. F. Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).
[6] H. Beutler, Zeits. f. physik. Chemie **B29**, 315 (1935).
[7] O. Oldenberg and A. A. Frost, Chem. Rev. **20**, 99 (1937).

adsorbed but suffer only elastic collisions with the hot surface do not usually remain on the surface long enough to be excited in the vibrational degrees of freedom and hence be decomposed in equilibrium amounts. For example, it has been shown by Schwab and Pietsch[8] in the case of methane and in this laboratory in the case of methyl chloride, that only about one in every thousand of these molecules comes to thermal equilibrium when colliding with a hot surface. Thus, it is probable that this complete attainment of thermal equilibrium is possible only for molecules and surfaces, between which, like hydrogen and tungsten, chemi-adsorption occurs. The halogens and oxygen on tungsten are probably other examples.

In view of the fact that observations seem to have been made only under equilibrium conditions it appears that they can shed no light on the postulated mechanism.[9] It seems safe to say only that the speed of the reaction on the surface is very much faster than the processes of adsorption and desorption and that this *may* be indicative of a mobile monolayer.

[8] G. M. Schwab and E. Pietsch, Zeits. f. physik. Chemie **121**, 189 (1926).

[9] Bryce and Roberts, Proc. Camb. Phil. Soc. **32**, 653 (1936).

Letters to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is the third of the month. Because of the late closing date for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not in general exceed 600 words in length.

The Extension of the Attractive Energy of a Solid into an Adjacent Liquid or Film and the Decrease of Energy with Distance

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October 19, 1943

ONE of the important, entirely unsolved problems of physics and chemistry is that of the distance to which the attractive energy of a solid extends into an adjacent liquid or film. The solution of this problem involves a determination of the variation of the energy of interaction with the distance. It might seem that the methods of theoretical physics might be applied to the calculation of the relationships involved but up to the present time no successful calculations have been made.

An experimental method which is capable of solving this problem within certain limits of error has been developed by the writers, and has been applied to a single case, while other cases will be investigated when the pressure of work more essential in the present emergency becomes less.

For many years there has been a wide divergence of opinion between those who consider that adsorbed films on the plane surfaces are monomolecular, and those who consider that they are polymolecular. For example, Langmuir in his Seventeenth Faraday Lecture "Monolayers on Solids" (December 15, 1938)[1] states that for films of argon, nitrogen, hydrogen, and methane, at liquid air temperatures "the amount adsorbed increases about in proportion to the pressure, but at higher pressures reaches a limiting value which in every case studied corresponds to less than a monolayer. Evidently, therefore, even with these cases of adsorption which involve merely van der Waals forces, the effective range of action of the forces responsible for the adsorption is less than the molecular diameter, so that we are still clearly dealing with forces which act between atoms or molecules in contact."

Brunauer and Emmett,[2] Emmett and Brunauer,[3] and Brunauer, Emmett, and Teller,[4] (BET), take a different point of view, since they consider that the film is polymolecular (for nitrogen at −195.8°C) at values of p/p_0 above about 0.1.

We have definite evidence that films of nitrogen at −195.8°C and of water at room temperature are polymolecular on many solids at the higher pressures. A part of this evidence consists of experimental values which show how the attractive energy between titanium dioxide, in the form of anatase, and water varies with the thickness of the water layer. From other work done in this laboratory it may be stated that the relations for quartz would be almost the same.

The experimental method which we use is based upon Eq. (4) of the following letter. Since the heat of vaporization of water is well known, it is necessary to determine only the energy of immersion (negative of the energy of emersion) for the clean solid, by a method described earlier, and of the solid covered by adsorbed films of different thickness.

The technique involves too many details to be described here, but Fig. 1 exhibits the type of apparatus employed. Six tubes F with equal weights of TiO_2 were used for a single set of experiments. The amount of water in the bulb H was determined by weighing on a semi-microbalance. Dry air in B, at an initial pressure of about 20 mm, was used to determine the free volume of the essential part of the apparatus.

Figure 2 gives the variation in the energy of emersion in erg cm^{-2} when water is adsorbed on a sample of TiO_2 which has an area of 13.8 sq. meters per gram as determined by our *absolute* method for the determination of area.[5] The application of the BET theory gives 13.9 meters^2 $(g)^{-1}$ on the basis of Emmett's usual assumption that the mean area per nitrogen atom is 16.2 A^2.

At the temperature used for this work (25°C), the heat

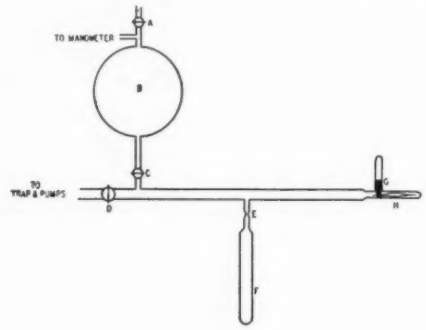

FIG. 1.

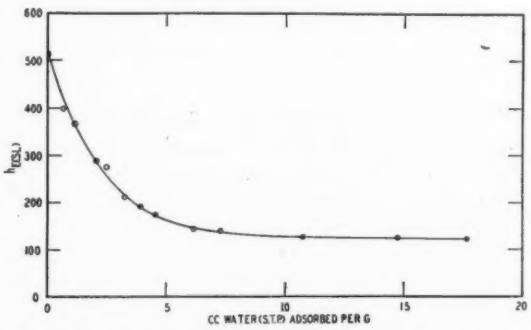

FIG. 2. Decrease in energy (erg cm^{-2}) of emersion of titanium dioxide (anatase) from water as the thickness of the water film increases. Values in cu cm of vapor for 1 g solid which has an area of 13.8 square meters.

of vaporization of water is 10,480 cal. mole^{-1}. The most convenient method of expressing our results seems to be to give the excess heat of desorption (or adsorption) per mole for each molecular layer, above that for water itself, or $H_{D(n)}-H_{D(\infty)}$.

The values are as follows (Table I) in calories per mole.

TABLE I.

Layer	$H_{D(n)}-H_{D(\infty)}$ or E_1-E_L	Values for exponential decay
1	6550	6550
2	1380	1637
3	450	409
4	80	102
5	40 (?)	26
All above 5	30 (?)	

With our calorimetric equipment the values for the fourth and fifth layers are very inaccurate, but it seems to be certain that the energy is not entirely negligible.

With nitrogen on various non-porous solids at −195.8°C, and with water on these solids at 25°C, we commonly obtain films which are from 7 to 10 monolayers thick before saturation is attained, that is, at pressure slightly *below* $p/p_0=1$. Since the areas are determined by our absolute method, it is certain that these adsorbed films are highly polymolecular, especially since the nitrogen molecule would have to occupy an area as low as 1.56A^2 to make the film monomolecular, while the lowest area we have ever obtained is 13.7A^2.

The values given in the table suggest that $H_{D(n)}-H_{D(\infty)}$ which is the BET E_1-E_L undergoes an exponential decay, as indicated by the last column. On this basis the experimental value for the second layer is too low, and for the third, too high, to meet this condition, which suggests an orientation effect in the layers. Unfortunately, the errors in the experimental values are so large that there is no evidence for this point of view.

[1] I. Langmuir, J. Chem. Soc., pp. 520–521 (1940).
[2] S. Brunauer and P. H. Emmett, J. Am. Chem. Soc. **57**, 1754 (1935).
[3] P. H. Emmett and S. Brunauer, J. Am. Chem. Soc. **59**, 310, 1553 (1937).
[4] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. **60**, 309 (1938).
[5] W. D. Harkins and George Jura, J. Chem. Phys. **11**, 430 (1943).

The Relationship Between the Energy of Adsorption of a Vapor on a Solid and of Immersion of the Solid in a Liquid

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October 19, 1943

THE heat of adsorption of a vapor upon the surface of a solid can in general be calculated more accurately from heats of immersion and condensation than by any direct or indirect experimental adsorption method. It is, therefore, unfortunate that the equations used in the literature to express the relationship between the energies of adsorption and immersion are universally incorrect.

If h is used to designate the increase in the Gibbs heat function per unit area, then

$$h=(\partial H/\partial\Sigma)_{T,p} \quad (\Sigma=\text{total area})$$

may be used as the definition of h. In the following derivation of the correct relationship between the heat of adsorption and the heat of emersion[1] $h_{E(SL)}$ is the heat of emersion of the clean solid from the liquid in erg cm^{-2}; $h_{E(S_fL)}$ is the heat of emersion in erg cm^{-2} of the solid, with n moles of adsorbed vapor per cm^2, to form a clean solid surface; λ is the heat of vaporization in erg mole^{-1}.

Consider a non-porous solid with an area of 1 cm^2 and a negligible volume. The following processes may be imagined to occur:

1. The solid is emersed from n_1 moles of liquid into a vacuum. Here n_1 is assumed to be large in comparison with the n moles considered in the next step.

$$\Delta H=h_{E(SL)}. \tag{1}$$

2. The solid is emersed from n_1 moles of liquid into the vapor of the liquid at the pressure p_1 carrying with it a film of just the correct thickness to give it equilibrium with the vapor *at this pressure*. The amount of liquid removed in this film is n moles.

$$\Delta H=h_{E(S_fL)}. \tag{2}$$

3. Of the n_1 moles of liquid left in (1), evaporate n moles, leaving (n_1-n) moles, which is the amount of liquid left in 2.

$$\Delta H=n\lambda. \tag{3}$$

Subtract 2 from 1+3, since this will give the increase in the value of the heat function when the film of n moles is vaporized (desorbed) from the surface of the solid.

$$h_{D(VS_f)}=h_{E(SL)}-h_{E(S_fL)}+n\lambda. \tag{4}$$

Now,

$$h_{E(SL)}=h_S-h_{SL} \tag{5}$$

$$h_{E(S_fL)}=h_{S_f}-h_{SL}. \tag{6}$$

So,

$$h_{D(VS_f)}=h_S-h_{S_f}+n\lambda \tag{7}$$

and since in general

$$h=\gamma-T(\partial\gamma/\partial T)_{p,T}, \tag{8}$$

where γ is the free surface energy per sq. cm

$$h_{D(VS_f)}=\gamma_S-\gamma_{S_f}-T[(\partial\gamma_S/\partial T)-(\partial\gamma/\partial T)]_{p,T}+n\lambda. \tag{9}$$

It has been customary to express the heat of adsorption either in cal. g^{-1} or cal. mole^{-1}. If it is wished to express the heat in cal. g^{-1} the result is

$$H_{D(VS_f)}=H_{E(SL)}-H_{E(S_fL)}+n\lambda, \tag{10}$$

where $H_{E(SL)}$ and $H_{E(S_fL)}$ are the heats of emersion in cal. g^{-1} of adsorbent and n is the number of moles of vapor adsorbed g^{-1}. If it is wished to express the result in cal. mole^{-1} of vapor adsorbed, the equation becomes

$$H_{D(VS_f)}=(1/n)[H_{E(SL)}-H_{E(S_fL)}]+\lambda. \tag{11}$$

Although the equations have been derived for a crystalline material, the results are equally applicable to porous materials.

The relationship that has been used is

$$H_{D(VS_f)}=H_{E(SL)}+n\lambda. \tag{A}$$

This equation was believed to be applicable only when the solid is saturated with the vapor. This formula has even received experimental "proof," which was obtained by using a porous adsorbent. In this case, the pores are filled with adsorbate. This reduces the area of the sample so that the second heat of emersion term becomes effectively zero.

Equation (4) is the fundamental equation for the calculation of the heat of desorption or its negative, the heat of adsorption. This equation is valid for either non-porous or porous solids at any value of p/p_0. In the literature of the subject, the term $-h_{E(S_fL)}$, which may have a considerable magnitude, is always omitted. This makes the equation entirely inapplicable to non-porous solids, and also to porous solids except at $p/p_0=1$, where it is *still incorrect*, but gives an approximation to the correct result. The error introduced by the omission of this term may be illustrated by calculations from the data of Razouk.[2] When his sample of charcoal had adsorbed 13.5 percent of that adsorbed at $p/p_0=1$, the heat of adsorption (q_a) was 9.9 cal. g^{-1}, while the omission of the term in question gives $q_a=22.4$ cal. g^{-1}.

[1] W. D. Harkins and H. K. Livingston, J. Chem. Phys. **10**, 342 (1942).
[2] R. I. Razouk, J. Phys. Chem. **45**, 190 (1941).

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